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RATES, CONSTANTS, AND KINETICS FORMULATIONS IN SURFACE WATER QUALITY MODELING

by

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FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient analytical tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement,transformation, impact, and control of environmental contaminants, the Technology Development and Applications Branch develops management or engineering tools to help pollution control officials achieve water quality goals through watershed management.

Basin planning requires a set of analysis procedures that can provide an assessment of the current state of the environment and a means of predicting the effectiveness of alternative pollution control strategies. This report contains a compilation and discussion of rates, constants, and kinetics formulations that have been used to accomplish these tasks. It is directed toward all water quality planners who must interpret technical information from many sources and recommend the most prudent course of action that will minimize the cost of implementation and maximize the environmental benefits to the community.

David W. Duttweiler
Director
Environmental Research Laboratory
Athens, Georgia

PREFACE

Over recent years, the number of water quality modeling studies has grown substantially. Conceptually, commonly used models (e.g., SWMM, QUAL) have undergone major revision and improvement, and through application, data on rate constants and coefficients have also proliferated. Yet, data and information on simulation approaches tend to be scattered among technical reports, journal articles, and government publications, and it is the need to consolidate such information which led to the preparation of this volume.

The document represents many months of work spent in reviewing models and application studies, compiling data, examining equations for validity, reviewing conceptualizations and, of course, seemingly endless editing. Yet, the work invested was nominal compared to the efforts of the thousands of researchers the results of whose labors are so summarily presented. It is those researchers to whom we are most indebted in the preparation of this manual.

A comment is in order here regarding works cited in this document. We have made every effort to provide appropriate citations acknowledging the reports, articles, and materials used. Yet, we observed several cases, especially with respect to figures, where materials were used in several reports without proper source citations. This made it infeasible to search to locate the original reference, and we regret that we were obliged to cite the specific report in which the figure was found, although it might not have been the primary reference.

Throughout the preparation of a document such as this, one thought has recurred to us time and again namely, how desirable it would be to have some feedback from users. We would like to know what proves useful, what areas of special interest have not been covered in sufficient detail, and what studies would be useful in expanding this kind of document in the future. If there is sufficient interest, it may be possible at a later date to expand coverage into additional areas of importance.

Finally, we would like to express our sincere hope that this document is both convenient and useful to water quality modelers. Every effort has been made to provide a balanced coverage, logical presentation and appropriate organization. Yet, the final test comes in actual application. This is why we hope users will provide us with both general and technically specific feedback. Such inputs will be most sincerely appreciated.

ABSTRACT

Recent studies are reviewed to provide a comprehensive volume on state-of-the-art formulations used in surface water quality modeling along with accepted values for rate constants and coefficients. Topics covered include system geometric representation (spatial and temporal), physical processes (mass transport, heat budgets, ice formation, light extinction), biological systems (fish, benthic organisms), and chemical processes (nutrient cycles, carbonate system). A detailed discussion is also presented on issues which are ordinarily of primary interest in modeling studies. These include reaeration, dissolved oxygen saturation, photosynthesis, deoxygenation, benthic oxygen demand, coliform bacteria, algae, and zooplankton. These discussions incorporate factors affecting the specific phenomena and methods of measurement in addition to data on rate constants.

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CONVERSION FACTORS

English Unit	Multiplier	SI Unit	English Unit	Multiplier	SI Unit
acre	X4.046.724→ ← 2.471X10^{-4}X	m^2	gpd/ft	X0.0124→ ← 80.[illegible]X	m^3/day m
acre	X0.405→ ← 2.471X	ha*	gpd/sq ft	X0.0408→ ← 24.51X	m^3/day m^2
acre-ft	X1,233.5→ ← 8.11X10^{-4}X	m^3	gpm	X0.0631→ ← 15.85X	dm^3/s
Btu	X1.055→ ← 0.9478X	kJ	gpm	X0.0631→ ← 15.85X	1*/s
Btu	X0.252→ ← 3.968X	kg-cal*	gpm/sq ft	X40.7→ ← 0.0245X	1*/min m^2
Btu/hr/sq ft	X3.158→ ← 0.316X	J/s-m^2	hp	X0.7454→ ← 1.341X	kW
Btu/1b	X0.555→ ← 1.80X	kg-cal/kg*	hp-hr	X2.684→ ← 0.372X	MJ
cfm	X0.028→ ← 35.71X	m^3/min	in.	X2.54→ ← 0.3937X	cm
cfs	X1.7→ ← 0.588X	m^3/min	1b/day/acre-ft	X3.68→ ← 0.2717X	g/day m^3
cfs/sq miles	X0.657→ ← 1.522X	m^3/min km^2	1b/1,000 cu ft	X16.0→ ← 0.0625X	g/m^3
cu ft	X0.028→ ← 35.314X	m^3	1b/day/cu ft	X16→ ← 0.0625X	kg/day m^3
cu ft	X28.32→ ← 0.0353X	1*	1b/mil gal	X0.92→ ← 8.333X	g/m^3
cu in.	X16.39→ ← 0.061X	cm^3	mil gal	X3,785→ ← 2.64X10^{-4}X	m^3
cu yd	X0.75→ ← 1.3709X	m^3	mgd	X3,785→ ← 2.64X10^{-4}X	m^3/day
^oF	0.555(^oF−32)→ ← 1.8(^oC)+32	^oC	mgd	X0.0438→ ← 22.82X	m^3/s
^oC	plus 273→ ← minus 273	K	mile	X1.61→ ← 0.621X	km
ft	X0.3048→ ← 3.28X	m	ppb	X10^{-3}→ ← 1,000X	mg/1*
ft-1b	X1.356→ ← 0.737X	J	ppm	approximately equal to	mg/1*
gal	X3.785→ ← 0.264X	1*	sq ft	X0.0929→ ← 10.76X	m^2
gal	X0.003785→ ← 264.2X	m^3	sq in.	X645.2→ ← 0.00155	mm^2
gpd/acre	X0.9365→ ← 1.068X	m^3/day km^2	sq miles	X2.590→ ← 0.3861X	km^2

Other commonly used conversions:

1 MGD = 1.55cfs	1 MW = 3.414 X 10^6 BTU/hr	1 BTU = 252 cal
γc_p = 62.4 BTU/ft^3/^oF	1 BTU = 778 ft-1b	1 Langley/day = 3.7 BTU/ft.^{2}/day

*Not an SI unit, but a term commonly used and preferred as a wastewater unit of expression.

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The authors would like to first thank Dr. Marc Lorenzen for providing technical guidance early in the study when goals and direction were being defined and such guidance was so vitally important. Dr. Lorenzen's input was especially useful in determining appropriate coverage and in collecting and organizing materials for review.

Thanks are due the participants in the Symposium on Rate Constants, Coefficients, and Kinetics formulations which was held in the San Francisco Bay Area from February 23-25, 1977, and whose inputs provided a significant part of the materials used in preparing this document. The authors would also like to acknowledge the efforts of Mrs. Anna Zison who provided all of the graphics work in redrawing figures from reports reviewed and providing several new ones, to Mr. Steve Gherini, and Mr. David Dykstra for their editing efforts, and to Mrs. Bernice Bujacich for preparing the drafts.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The use of mathematical models to simulate ecological and water quality interactions in surface waters has grown dramatically over the past decade. To some extent, the recent increase in the use of models as well as in model development is attributable to Section 208 of PL92-500, the Water Pollution Control Act Amendments of 1972. To meet the requirements of Section 208, which calls for areawide wastewater planning in both designated and nondesignated areas across the United States, 208 planners have often found that simulation techniques offer the best course for evaluating wasteload abatement alternatives. Predictions of system behavior based upon mathematical simulation techniques may be misleading, however, particularly if the physical mechanisms involved are not accurately reflected in the model. Furthermore, even where the model does faithfully describe mechanisms in the prototype, poor results may be obtained where insufficient data are available to estimate rate constants and coefficients.

Much of the recent work done in the water quality modeling field has been oriented toward improvement of models--toward incorporating better numerical solution techniques, toward an expanded complement of water quality constituents simulated, and toward realistic representations of modeled physical, chemical, and biological phenomena.

In contrast, although a substantial body of data has been developed on rates and coefficients for use in the various important models, the data are scattered throughout journal articles, government documents and technical reports. This, of course, makes it difficult for the modeler to obtain necessary guidance in assigning values to the various constants and coefficients required by his model. The solution has commonly been to gather data with which to estimate the coefficients or to undertake a time consuming literature search--expensive in either case.

Recognizing these problems, the United States Environmental Protection Agency and Tetra Tech, Inc. sponsored a symposium in the San Francisco Bay Area, entitled "Rate Constants, Coefficients, and Kinetics Formulations in Surface Water Modeling." The symposium was held on February 23 through February 25, 1977. It was a major step in the preparation of a single, comprehensive compilation of data on surface water quality modeling formulations, and values for rate constants and coefficients. In addition to the symposium, and also supported by U.S. Environmental Protection

Agency funds, an extensive literature search was undertaken to provide background material for the manual to be prepared. This document represents the culmination of these efforts, and it is hoped a substantial beginning in the solution of difficulties inevitably encountered by modelers when they attempt to select appropriate values for model parameters.

1.2 SCOPE AND ARRANGEMENT OF MANUAL

In preparing this manual, an attempt has been made to present as comprehensive a set of formulations and associated constants as possible. Guidance in the selection of topics has been provided primarily by the extent of use by workers in the field instead of through a critical assessment of technical validity. Rather than exclude some methods, the philosophy has been to present arguments for and against any controversial approach.

The manual is divided into three chapters. Following this introductory chapter, Chapter 2 is largely a literature review covering a broad spectrum of processes and formulations. The arrangement is:

- Model conceptualization
- Physical processes
- Biological processes
- Chemical processes
- References.

Chapter 3 contains a very detailed discussion of selected parameters and formulations not included in Chapter 2. Topics relegated to Chapter 3 include those which, it was felt, would be of greatest interest to the reader, and about which questions most often arise. Chapter 3 includes discussions on the following subjects:

- Reaeration
- Phytoplankton
- Zooplankton
- Biochemical oxygen demand
- Coliform bacteria
- Benthic oxygen demand
- Dissolved oxygen saturation
- Photosynthesis (without modeling phytoplankton).

References for the various discussion topics are included at the end of each section.

1.3 SOME GENERAL OBSERVATIONS

In the course of compiling this manual, several issues arose which warrant discussion here. First, each rate value or expression used in a model should not be chosen as an "afterthought," but should be considered as an integral part of the modeling process. A substantial portion of any modeling effort should go into selecting specific approaches and formulations based upon the objectives of modeling, the kinds and amounts of data available, and the strengths and weaknesses of the approach or formulation. Once formulations have been selected, a significant effort should be made to determine satisfactory values for model parameters. Even where the parameter is to be "calibrated," it is clearly important to establish whether the calibrated value is within a reasonable range or not. Further, it should always be remembered that the value of any constant or coefficient is dependent upon the way it is used in the formulation.

Second, there is rarely consensus on how best to select a particular rate, coefficient, or expression for a given prototype. Generally, there are a great many environmental factors influencing a given rate parameter. The factors can be complex, and as a result, may be poorly understood, and their influence on rate constants inadequately quantified. In some cases, such as in modeling stormwater runoff quality, there may be so many physical and chemical factors involved in the prototype that developing a satisfactory mechanistic model may be impractical or beyond the "state of the art." Furthermore, it is not uncommon for researchers to disagree on both the direction and extent to which a particular physicochemical or biological factor influences a given rate. Accordingly, further study on rates of various surface water phenomena is certainly to be encouraged.

Third, based on the commonly large differences in observed rates from system to system, some researchers believe that some surface water quality parameters are highly system-specific. Accordingly, it may be difficult to establish or use general rate constant selection guidelines. It is apparent, however, that so long as the phenomena modeled are basically mechanistic rather than stochastic in nature, the key to intersystem generality lies in understanding and quantifying the actual determinative factors and causal relationships influencing the process modeled. It may be that apparent system specificity of rate constants is only a manifestation of the researcher relying on too few and/or incorrectly selected predictive variables.

Fourth, modelers should be keenly aware of the range of applicability of a particular expression or value, conditions under which the field measurement technique is valid, and the limitations of both the expression and the measurement technique. However, a simplified representation of the prototype is often adequate where proper constraints are placed on temporal or spatial conditions of the simulation. For example, a linear estimate may be a sufficient representation of a nonlinear phenomenon if the range over which the phenomenon is simulated is carefully selected.

Fifth, there is currently some disagreement among researchers as to whether there is a need for increased model sophistication, particularly where simulation of complex ecosystems are concerned. On the one hand, by making ecosystem representations more sophisticated, the number of model parameters almost certainly will increase. Since it is likely that many of the new parameters may be understood only qualitatively, the new, more sophisticated model may be less reliable and accurate than the older version. On the other hand, however, some systems and phenomena represented in existing models (e.g., fish, pesticide transport, runoff water quality) are so complex in nature that unless these models are made more detailed and realistic, there is often little reason to believe that good simulations are other than fortuitous.

Finally, a comment is in order here regarding assumed singularity of constants, coefficients, and results of simulations. In general, in modeling studies, a narrow range of values or even a single value for each model coefficient is selected and used, and a single estimated value for each parameter is determined as a function of time and location within the prototype. Similarly, in field studies and in interpretation of physical, chemical, and biological data, individual values are taken as precisely representing actual conditions when, in fact, all of the data and coefficients represent samples drawn from large populations. Although costs usually preclude advanced statistical analysis and delineation of population parameters for all input and, consequently, output of modeling studies, it is important that the fact that model output also represents a sample from a large population be kept in mind. The ramifications of this are very important. What may appear to be an excellent calibration or an excellent simulation may, in fact, be well outside the envelope of expected values based on field conditions (if these conditions were known). Conversely, what appears to be a poor simulation, and what might lead to extensive reworking and rethinking of the adopted model, may be more a manifestation of a large dispersion in field data than mathematical misrepresentations of underlying physical mechanisms. Accordingly, the importance of visualizing input data and the resulting output as a sample from a larger population must be stressed.

1.4 USE OF THIS MANUAL

This document is intended for use as a handbook--a convenient reference on modeling formulations, constants, and rates commonly used in surface water quality simulations. It was impossible to encompass all formulations or to examine and discuss even the majority of recent reports containing rates data. It is hoped, therefore, that the user will recognize the desirability of seeking additional sources where questions remain about formulations or values. Data used from within this volume should be recognized as representing only a small sampling from a much larger set of data. It should also be noted that there are very real limitations involved in using literature values for rates rather than observed system values. It is hoped, finally, that this document will find its main use as a guide in the search for "the correct value" rather than as the sole source of that value.

CHAPTER 2

A PROCESS-ORIENTED LITERATURE REVIEW OF RATE PARAMETERS USED IN SURFACE WATER QUALITY MODELS

2.1 INTRODUCTION

The objective of this chapter is to present the results of a literature survey which reviewed ecological modeling studies. The surveyed literature emphasized recent works in which lakes, rivers, and estuaries were simulated. Mathematical models used in studies of this type generally consist of a set of equations that describe water and waste movement within the water column, together with appropriate boundary conditions and empirical parameters. The models cited were examined in terms of adopted simplifications and the assumptions under which each is appropriate. Emphasis was placed on gathering information concerning rate constants, coefficients, and kinetics formulations used in these models of water systems.

The kinetics formulations and associated rate parameters reviewed in this chapter are grouped according to the kind of phenomena represented. The categories are physical, chemical, biochemical, and biological processes. Although the subdivision is admittedly artificial, it does provide a convenient basis for organization and allows for a logical flow from topic to topic. In some cases, it has been difficult to select the proper niche for a particular topic, but it is hoped the arrangement will nevertheless prove convenient to the user.

Emphasis in this chapter is on model conceptualization, followed by a fairly detailed coverage of formulations and parameters which, though important, are not necessarily in the very general mainstream of ecological modeling. Formulations and issues warranting special emphasis have been relegated to Chapter 3.

2.2 MODEL CONCEPTUALIZATION

2.2.1 Geometric Representation

Model design is, by its nature, a pragmatic process--the simulation objectives determine the basic form of the model, and then the mathematical system description and solution techniques are formulated. In developing the system description, several major issues must be addressed. These include:

- What kind of spatial representation is needed to accurately describe the prototype?

- What temporal scale should be used?

- Should the model be dynamic or is a steady-state approximation adequate?

- What kind of kinetic formulations are most appropriate to describe the time-based changes in pollutant concentrations?

In addressing these issues, it is reasonable to begin with the spatial representation. Normally, the first step is to divide the water body into a series of volume elements or segments, such that spatial homogeneity is attained without violating mathematical requirements or posing unnecessary computational complexity. Ideally, the proper segmentation of the system allows for a realistic portrayal of both advective and dispersive transport. It also permits inclusion of chemical and/or biological kinetics where water quality is to be modeled. Invariably, the resulting spatial representation is a compromise considering these criteria, the capacity of computational facilities, and other resources available.

In water quality modeling, the ideal description of the pollutant concentration field would be a continuous accounting of concentrations at all points throughout the system. That is, the instantaneous concentration of each pollutant, $\mathbf{C}_p$ would be defined as a function of spatial location (x, y, z axes) and time (t):

$$C_p = f(x,y,z,t) \qquad (2\text{-}1)$$

It is obviously infeasible to compute the infinite set of C_p. Fortunately, however, feasible representations, often using fewer than three spatial ordinates and discrete time steps, have proven satisfactory in most applications.

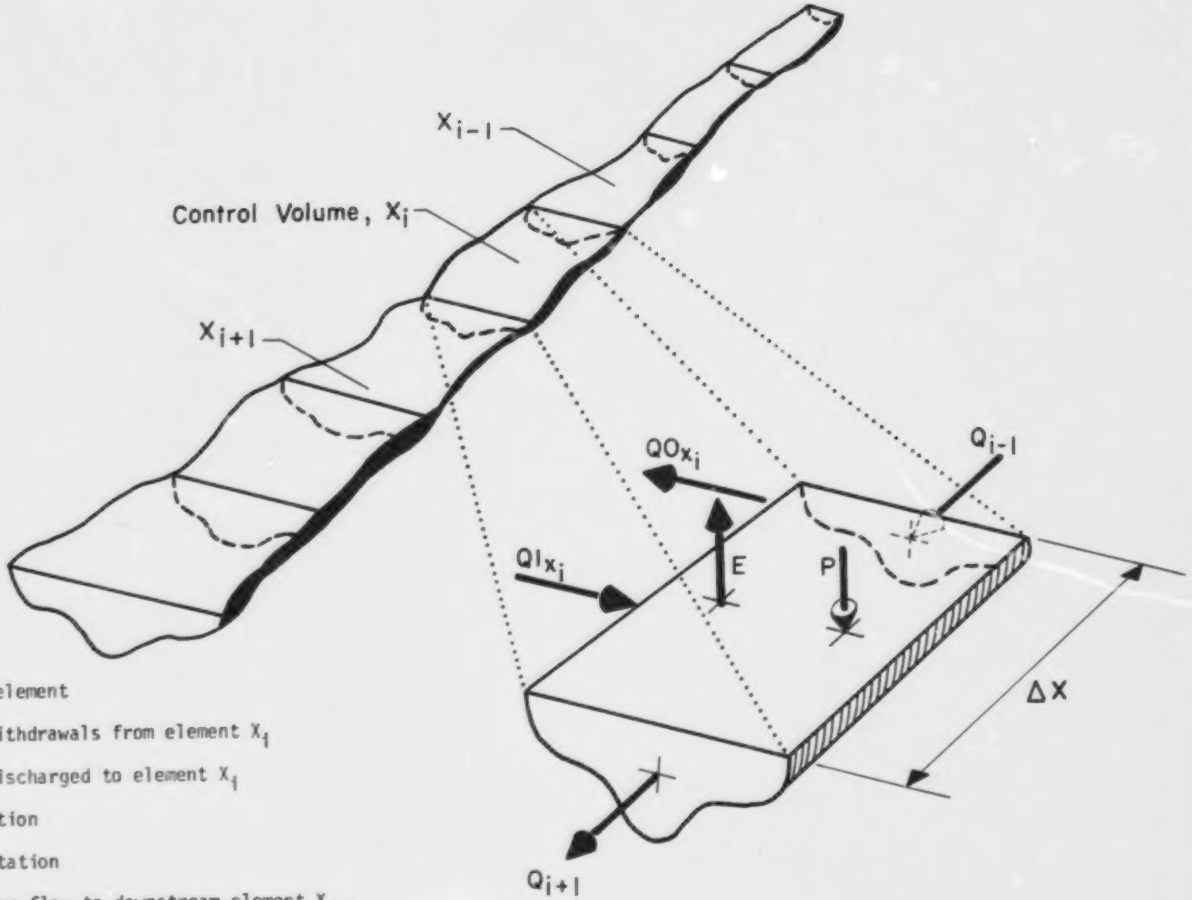
2.2.1.1 Zero-Dimensional Models

Zero-dimensional models are used to estimate spatially averaged pollutant concentrations at minimum cost. These models predict a concentration field of the form $C = g(t)$, where t represents time. They cannot predict the fluid dynamics of a system, and the representation is usually such that an analytical solution is possible.

As an example, the simplest representation of a lake is to consider it as a continuously stirred tank reactor (CSTR). For such a coarse representation, the model generally cannot adequately simulate seasonal algal growth dynamics. Such models are often used for nutrient budget computations using an annual time step.

2.2.1.2 One-Dimensional Models

Most river models use a one-dimensional representation, where the system geometry is formulated conceptually as a linear network of segments or volume sections (see Figure 2-1). Within each segment, the water is assumed to be completely mixed, so that there is no water quality variation laterally



X_{i-1}
Control Volume, X_i
X_{i+1}
QO_{x_i}
Q_{i-1}
QI_{x_i}
E
P
ΔX
Q_{i+1}

X_i = volume element
QO_{x_i} = water withdrawals from element X_i
QI_{x_i} = water discharged to element X_i
E = evaporation
P = precipitation
Q_{i+1} = advective flow to downstream element X_{i+1}
Q_{i-1} = advective flow from upstream element X_{i-1}
ΔX = longitudinal dimension of element

Figure 2-1. One-dimensional geometric representation for river systems (Chen and Wells, 1975).

or with depth. Variation occurs longitudinally (in the x-direction) as the water is transported out of one segment and into the next. These river models thus calculate the horizontal water quality profiles along a river system, considering each segment as a CSTR.

As one-dimensional stream models have become relatively sophisticated, the number of phenomena simulated, both in terms of hydrology and water quality, has grown substantially. Early models, such as DOSAG, considered only DO and BOD. QUAL-II, a model developed over the years by Water Resources Engineers and the Texas Water Development Board, simulates roughly 20 constituents and will accommodate 90 reaches of up to 20 CSTR's each. A more recent one-dimensional river model employed for a study of the Kings River, California by Tetra Tech (1976) is similar in capability to QUAL-II. It utilizes a river system representation which includes tributary branches. At any section of the river, this model accepts reservoir releases, natural runoff, and diverted flows. The river can also receive discharges from a power plant and water can be diverted for power generation.

For lakes exhibiting stratification and long residence times, a one-dimensional approach in which the water body is represented by a stack of horizontal slices or layers (Figure 2-2) has been used extensively (Lombardo, 1972, 1973; U.S. Army Corps of Engineers, 1974; Chen and Orlob, 1975; Thomann, et al., 1975; Tetra Tech, 1976b). Two-layer, three-layer, and multiple-layer representations have all been used in one-dimensional lake system applications (Chen, 1975). Within each slice or layer, the properties of water are assumed to be completely uniform. This type of representation assumes that the temperature gradients exist only along the vertical axis.

One-dimensional estuary representations, similar to the one-dimensional river systems, imply that the estuary is well-mixed vertically and laterally. According to Callaway (1971), "borderline" cases are not at all uncommon and assumptions of one-dimensionality for estuarial systems should be made cautiously.

Setting the number of horizontal segments* to be used in a one-dimensional estuarine simulation is a complex issue. Important considerations include the homogeneity of the water mass, the variations in physical, chemical, and biological parameters, the distribution of inputs along the length of the estuary, and the desired simulation accuracy. In addition, the tidal influences are a significant consideration in estuary systems, whether simulations are performed on a real-time or tidally-averaged basis. Real-time means that the hydrodynamics of each tidal cycle are actually simulated. Tidally averaged models consider only net flow, generally over a standardized tidal cycle, and incorporate a tidal dispersion coefficient to simulate flushing.

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*"Horizontal segments" will be used in this document to mean segmentation in the sense shown in Figure 2-1.

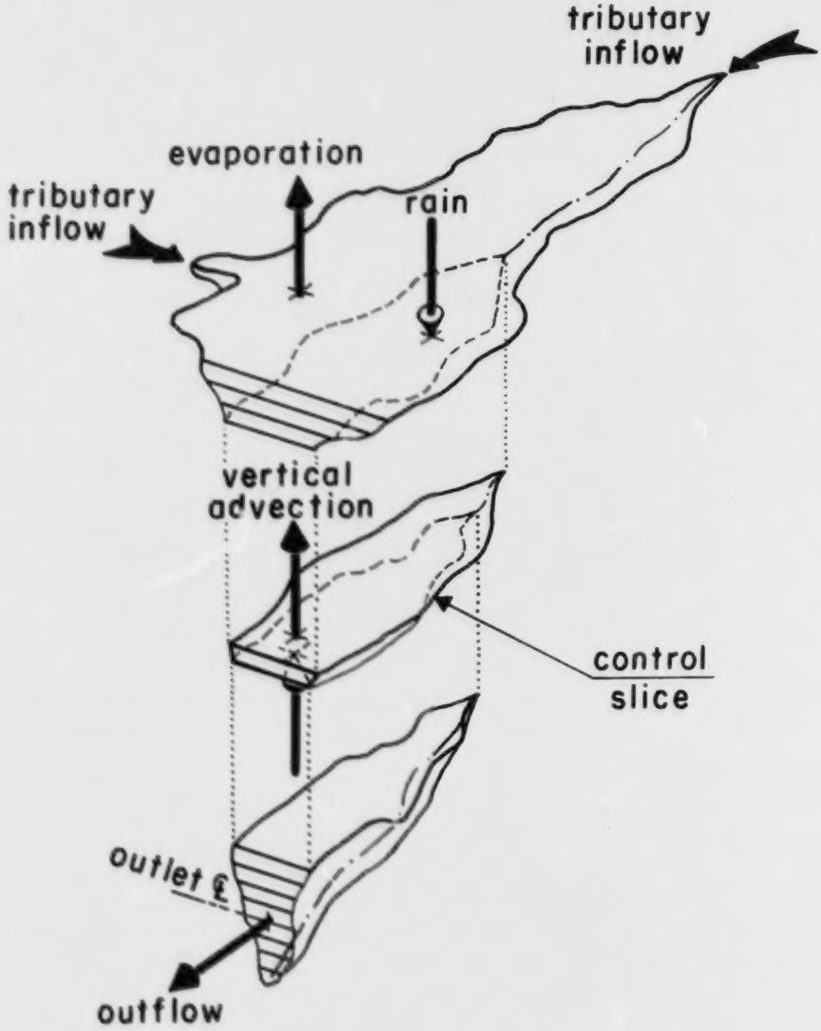
tributary
inflow
evaporation
tributary
inflow
rain
vertical
advection
control
slice
outlet ℄
outflow

Figure 2-2. One-dimensional geometric representation for lake systems (U.S. Army Corps of Engineers, 1974).

2.2.1.3 Two-Dimensional Models

A wide variety of two-dimensional conceptualizations of lake systems have been employed. Baca and Arnett (1976) have considered a quasi-two-dimensional approach, first longitudinally segmenting the lake and then considering each segment to be vertically layered (see Figure 2-3). The Fisheries Research Board of Canada (Lam and Jacquet, 1976, and Lam and Simons, 1976) has applied a one-layer, two-dimensional computer model which describes the complete longitudinal and lateral pollutant concentration regime while assuming homogeneity in the vertical direction.

The physical definition of an estuarine system restricts, to a large degree, the type of geometric representations which may be used. Most commonly, estuarine geometry is represented in mathematical models by a two-dimensional or quasi-two-dimensional approximation.

One particular quasi-two-dimensional approach that has been used extensively is sometimes referred to as a "link-node" system (see Figure 2-4) (Feigner and Harris, 1970; Crim and Lovelace, 1973; Chen and Orlob, 1975; Tetra Tech, 1976a). A "link-node" network may be constructed to represent a two-dimensional embayment, a system of discrete estuarine channels, or combinations of channels and shallow bays. The estuarine water body is subdivided into discrete volume units or "nodes." Nodes are characterized by surface area, depth, volume, and in some instances, side slopes. Nodes are interconnected by channels or "links." Links are defined by length, width, cross-sectional area, hydraulic radius (depth), and friction factor. Water is constrained to flow from one node to another through the defined channel. While the network is comprised of these one-dimensional channels, the representation is quasi-two-dimensional in that the description of quality provided is essentially two-dimensional (Figure 2-4).

Several other two-dimensional modeling approaches are coming out of the experimental stages and into operational use (Nihoul, 1975). Callaway (1971) reports an estuarine model developed by Leendertse that is capable of simulating two-dimensional, vertically integrated cases. Hinwood and Wallis (1975b), in their review of tidal models, report the use of two-dimensional side elevation models laterally averaged in density stratified estuaries, where the transverse variation in waste concentration is much smaller than the longitudinal and vertical variations.

2.2.1.4 Three-Dimensional Models

Three-dimensional spatial representations have been used to model overall lake circulation patterns. Until recently, much of the work on predicting circulation in lakes dealt with the overall hydraulic flow regime and not specifically with the nearshore area. A recent development which has contributed significantly to three-dimensional model conceptualization has been the use of a variable grid for the physical representation of a large lake. Several investigators (Chen, 1975; Tetra Tech, 1975; Lick, *et al.*,

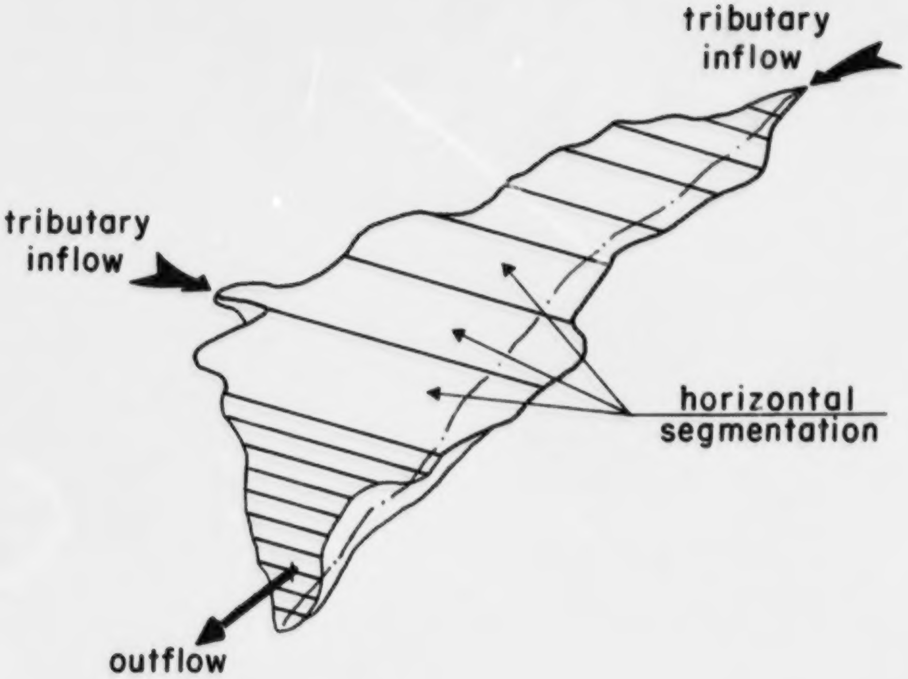
tributary inflow
tributary inflow
horizontal segmentation
outflow

Figure 2-3. Two-dimensional geometric representation for lake systems (Baca and Arnett, 1976).

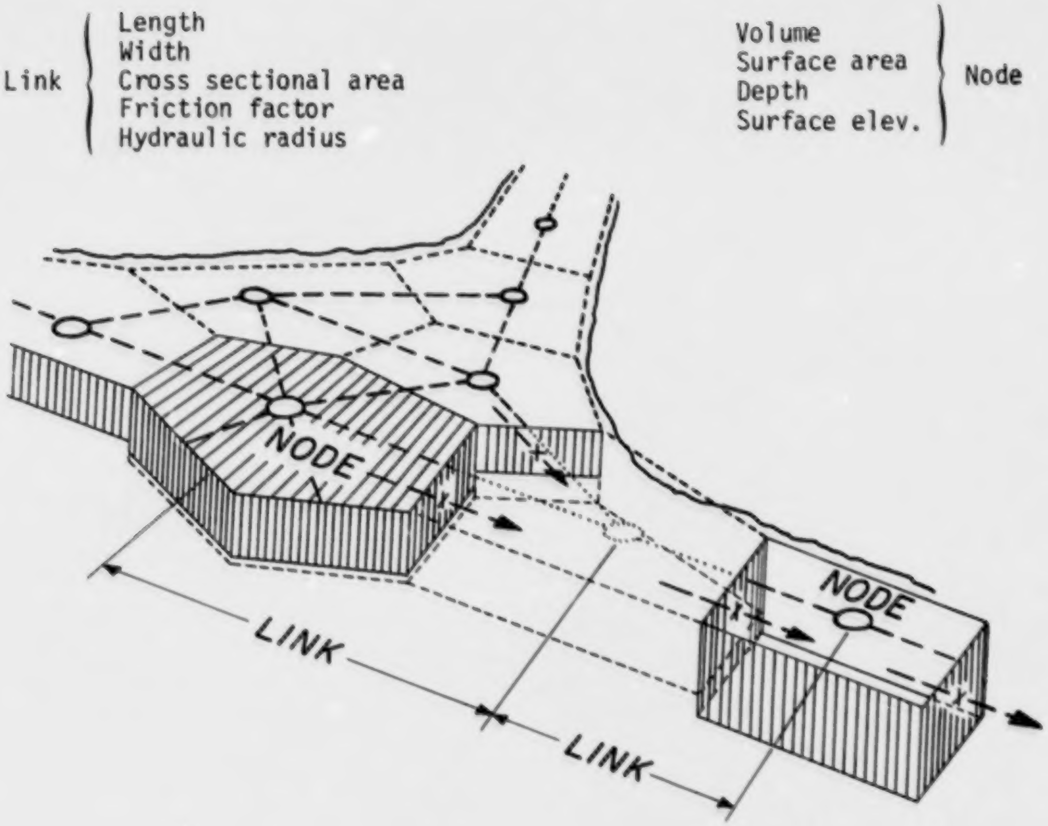
Link
Length
Width
Cross sectional area
Friction factor
Hydraulic radius
Volume
Surface area
Depth
Surface elev.
Node
NODE
NODE
LINK
LINK

Figure 2-4. Pseudo-two-dimensional geometric representation for estuary systems (redrawn from Orlob, 1974).

1976) have proposed such systems where detailed horizontal spatial description is provided for nearshore zones, and in the central core of the lake, where variation in the vertical direction is more important, larger horizontal segments with more numerous vertical layers are used.

The variable size grid employed in the hydrodynamic model can also be used with a water quality model which utilizes either the same spatial representation or a less detailed one having selected elements in common with the hydrodynamic model. Nihoul (1975) reports that three-dimensional computations for estuaries are now being approached by using finite difference approximation, and also by analytical solutions of the vertical velocity field.

2.2.2 Temporal Variation

Water quality models may be distinguished according to the temporal scale used. The current state of modeling places an emphasis on short-term responses of the ecosystem as opposed to the longer term responses.

2.2.2.1 Long-Term vs. Short-Term Models

The "long-term" models generally rely on a simplified geometric representation and simplified expressions for complex biological processes. This type of model has been useful in predicting long-term changes that result from increased or decreased nutrient loading rates (Tetra Tech, 1975; Lorenzen, et al., 1976). Long-term models may also be useful in predicting chronic problems which are slow to develop within an ecosystem.

"Short-term" models, which this review emphasizes, have been used to identify and solve acute pollution problems. Models of this type simulate a shorter time span than the long-term models, quite commonly emphasizing from diurnal to seasonal variations in system constituents. Such models provide an understanding of the behavior of the quality indices and of the aquatic ecosystem.

2.2.2.2 Dynamic vs. Steady-State Models

Ecological models are further distinguished on a temporal basis as being either "dynamic" or "steady-state." A strict steady-state assumption implies that the variables in the system equations do not change with time. Forcing functions, or exogenous variables, that describe environmental conditions which are unaffected by internal conditions of the system, have constant values. Inflows and outflows are discharged to and drawn from the system at a constant rate and any other hydrologic phenomena are also steady. Insolation, light intensity, photoperiods, extinction coefficients, and settling rates are a few examples of additional forcing functions which are held constant in a steady-state model. Constant forcing functions represent mean conditions observed in a system, and therefore the model cannot simulate cyclic phenomena.

A wide variety of planning problems can be analyzed by use of steady-state mathematical models which provide the necessary spatial detail for important water quality variables. Certain phenomena can achieve steady-state conditions within a short time interval and therefore can be modeled rather easily. Steady-state representations are particularly useful because of their simplicity. Examples of phenomena which have been modeled on a steady-state basis are: 1) bacterial die-off, 2) dissolved oxygen concentrations (under certain conditions), and 3) nutrient distribution and recycle.

The assumption of steady-state conditions may also be imposed in order to observe system response to extreme conditions (e.g., low summer flows). In these simulations, once steady-state has been reached, it persists indefinitely because the controlling variables all remain constant. In such cases, when arbitrary initial conditions are imposed, the output of the model can be used to determine when the system has reached steady-state. Linear programming concepts are also often used in conjunction with steady-state simulations to ensure certain water quality standards are met a given percent of the time at the least expense to the dischargers involved. Kelly (1975) reports of such an application to the Delaware Estuary. Long-term models are pseudo steady-state formulations, with a time step of computation on the order of months to a year (Tetra Tech, 1975).

In estuarine steady-state models, the effect of tidal height variations on cross-sectional areas (and hence on water volume changes) and tidal current fluctuations are not simulated. A steady-state estuarine model will predict waste concentrations corresponding to steady inflow and unvarying tidal conditions. Hinwood and Wallis (1975b) note that this type of model is unsatisfactory in short estuaries. Steady-state estuarine models are also unsatisfactory if the waste loads, river inflows, or tidal range vary appreciably with a period close to the flushing time of the area of interest.

The majority of dynamic models for rivers and lakes are concerned with eutrophication and its control. Thus the seasonal distribution of certain biological species and related abiotic substances is of major importance. The time step used in these models is on the order of one day or less for water quality computations (Hydroscience, 1971; Lombardo, 1973; U.S. Army Corps of Engineers, 1974; Tetra Tech, 1975; Chen and Orlob, 1975; Baca and Arnett, 1976; Tetra Tech, 1976b; Bierman, 1976; Simons, 1976).

The influence of tides in an estuary system poses a special problem in dynamic simulations. The hydrodynamic simulation must often be carried out with smaller time steps than the water quality computations to ensure computational stability (Hydroscience, 1971; Simons, 1976). If an intratidal model is used, the time step is largely governed by the grid spacing and the numerical formulation on which the model is based and is usually from 5 to 20 minutes. Time steps longer than about 30 minutes require more complicated numerical formulations to avoid averaging over the tidal period in an incorrect manner (Hinwood and Wallis, 1975a).

Stability criteria for estuary models are generally expressions which include channel length (indicative of grid spacing) and the celerity of shallow waves (Battelle, 1974; Tetra Tech, 1976a). Battelle (1974) used the following stability criteria in its estuarine simulation:

$$\Delta t = L \Big/ \left[V \left(1 + \frac{g n^2 L}{2.2 R^{4/3}} \right) + \sqrt{gR} \right] \qquad (2\text{-}2)$$

where Δt = maximum allowable time step, seconds

L = channel length, feet

V = channel velocity, feet/sec

R = hydraulic radius, feet

n = Manning's n, feet$^{1/6}$

g = gravitational constant, ft/sec^2

In certain instances, "quasi-dynamic" estuarine models have been used successfully (Crim and Lovelace, 1973; Tetra Tech, 1976a). In these models the quality equations are effectively integrated over time, assuming net, steady-state flows. The tidally averaged models use a tidal cycle as the basic time step and yield average daily results.

Another approach used in estuarine simulations is to solve for the quality interactions based on a "dynamic steady-state" hydraulic condition predicted in the hydraulic program (Feigner and Harris, 1970). In this approach, flows and heads are determined in a separate hydraulic subroutine and averaged for the larger time step used in the water quality model. These condensed hydraulic parameters for the full tidal cycle are stored on tape or disk for input into the quality program and thus are the basis for any number of quality runs. The quality solution proceeds over a full tidal cycle at which point the hydraulic input tape is rewound and used again as the basis for the next cycle.

The dynamic steady-state solution can be useful in estimating the flushing time for either continuous or instantaneous releases of pollutant. For the continuous case, after the pollutant has been distributed by allowing the program to run long enough (i.e., once dynamic steady state has been achieved), the given distribution at a given time, t, is simply used as the initial distribution (t=0) on a second run. The waste input is set to zero and the concentration decrease is recorded. To simulate the flushing of an instantaneous release, the initial distribution in a given section or grid of the model is set for a short time at a certain level and the program runs with no further input required.

2.2.3 Hydrodynamic Considerations

Virtually all water quality simulation models are based on the conservation of mass and the interaction of constituents. In general terms, the mass rate of change of a constituent, c, in any system segment may be written as (O'Connor, et al., 1975):

$$V \frac{dc}{dt} = J \pm \Sigma R \pm \Sigma W \qquad (2\text{-}3)$$

where R = chemical and biological transformation rates within the segment

W = rates of input to and withdrawal from segment

J = transport rate through segment

The latter two terms are sometimes combined within a single source-sink term. In order to solve Equation (2-3) the transport term, J, must be known. It is the purpose of the hydrodynamic model to determine J.

One of the most important questions which must be answered when formulating a modeling approach for a specific problem application, is the rigor with which the hydrodynamic processes must be represented in the model. This determination is made in conjunction with the geometric representation and temporal scheme chosen and is governed primarily by the same considerations. Generally two options are available to represent prototype hydrodynamics.

The most sophisticated approach is to compute the velocity field in a separate hydrodynamic model. Hydrodynamic models are primarily used in conjunction with water quality models containing detailed spatial representations. Hydrodynamic models can also be used in geometric representations of less than three spatial dimensions, however. For example, if a vertically averaged, two-dimensional representation is used, empirical resistance coefficients are used to represent vertical shear stresses and the turbulence effects are averaged over depth. When a separate hydrodynamic model is used, the flow field information which is computed must be retained for input into the water quality mass balance expressions.

This process of data transfer from the hydrodynamic to the water quality model is most easily accomplished if the same geometric grid is used for both model simulations. Frequently, however, the use of the identical grid is not practical because the hydrodynamic model grid may provide more detail than required for the water quality simulation. In these cases, it is the usual practice to provide a separate, less-detailed water quality grid, which may easily incorporate the hydrodynamic model output. This procedure requires the inclusion of a more sophisticated data exchange mechanism, but saves computational time in the water quality model.

The actual type and amount of data which are passed from the hydrodynamic model to the water quality model will vary with the particular application and investigation. A set of values is required which will describe the velocity field throughout the system. Generally, this means enough information to define the advection process.

The second approach to hydrodynamic simulation, which may be particularly advantageous in certain applications, is to input velocity values describing the circulation patterns directly into the water quality model. This approach may be used in water quality models at all levels of spatial detail. Often, circulation information is available from previous studies on the same prototype system. Depending on the needs of the application, previous results may suffice entirely or may be supplemented with additional data. Supplemental data can usually be obtained by direct measurements in the prototype system. The cost of this additional in situ sampling compared with the cost of alternative means of hydrodynamic simulation might determine the approach taken.

Due to the physical nature of typical estuaries, even the simplest of geometries often requires relatively sophisticated hydrodynamic information to accurately describe mass transport. The hydraulic behavior of estuaries and other coastal waters are usually influenced significantly by ocean tides and by the freshwater inflow to the system, in addition to the shape of the estuary. Coriolis and wind forces may also be significant in certain estuarine systems.

In modeling the hydrodynamic behavior of an estuary, the problem is essentially one of solving the equations describing the propagation of a tidal wave through a shallow water system. In an estuary, the principle features to be reproduced by the model are flow velocities and tidal stages induced by the river flow, the tidal currents, and the dispersion effects.

2.2.4 Solution Techniques

Mass balance expressions are formulated as differential equations, to be solved for each hydraulic element and for each of the quality constituents considered. In general a mass balance differential equation includes advection, diffusion, input, output, and sources and sinks. Where microorganisms are involved, for example, the metabolic processes of growth, respiration, and mortality can become the sources and sinks. A typical water quality model is composed of a set of simultaneous nonlinear, partial differential equations in both time and space. In order to solve these equations, it is usually necessary to resort to numerical solution techniques.

A specific method of solution, which was used in the majority of the water quality models reviewed in this study, is known as the finite-difference technique. In a finite-difference approach, the equations are integrated by approximating the actual solution with small forward time steps of finite dimension. For example, to integrate a basic differential equation over time the following approximation to the constituent concentration can be used for each element (U.S. Army Corps of Engineers, 1974):

$$C_{t+\Delta t} = C_t + \frac{\Delta t}{2}\left(\dot{C}_t + \dot{C}_{t+\Delta t}\right) \tag{2-4}$$

where $C_t, C_{t+\Delta t}$ = values of the dependent variable (typically concentration) at the beginning and end of the integration, respectively

$\dot{C}_t, \dot{C}_{t+\Delta t}$ = values of the rate of change of the dependent variable at the beginning and end of an integration interval, respectively

Δt = length of integration interval

Because of the complexity of the processes affecting the concentration c, the set of simultaneous differential equations are usually interdependent. Therefore, it is often required that the solution of one equation be available for computation in the next. Generally, a recursive scheme is established to integrate the equations with respect to time. Judicious selection of a solution order for the differential equations minimizes the ordering impact on the solution. Quite commonly, all constituent concentrations are computed sequentially for the hydraulic elements for each time step (Chen and Orlob, 1975). Then after all elements have been considered, another step forward in time is taken, and the computation process is repeated.

The finite difference approach can use either an implicit or an explicit solution technique. In an implicit solution the variables and their derivatives are both considered unknowns and are determined simultaneously. A commonly employed implicit solution technique is based on the Thomas algorithm, an adaptation of Gaussian elimination (Tetra Tech, 1975; Baca and Arnett, 1976).

The implicit technique is contrasted with explicit methods in which the derivatives (or the differential terms) are evaluated before the projections of concentrations are made. Callaway (1971) reports that trouble often arises in explicit methods of solution because of the short time periods required to ensure stability as well as a problem of conservation of mass. With regard to conservation of mass, momentum conservation can be violated resulting in abnormal velocity and water transport volumes. Often, modified explicit solution techniques, such as a "leap frog explicit solution" are used, which add a degree of accuracy and stability. Implicit methods of solution, on the other hand, although they tend to ensure stability, may introduce inaccuracies.

A slight preference for the implicit method of solution over the explicit method has been shown by investigators in water quality models. Baca and Arnett (1976), Chen and Orlob (1975), and the U.S. Army Corps of Engineers (1974) all use implicit solution techniques for their finite-difference schemes. Lombardo (1973) and Harper, as reported by Hydrocomp (Lombardo, 1972), employ explicit finite-difference solutions.

Another type of numerical solution technique, the finite element method, originally developed for structural analysis applications, has recently been applied quite successfully in several water quality modeling studies. Callaway, et al. (1971, 1976), constructed a finite element formulation for the geometry of the Columbia River system. Significant advantages to be gained from use of the finite element method are in its flexibility to more accurately portray boundary conditions and improved numerical stability.

2.3 PHYSICAL PROCESSES

2.3.1 Advective Transport

The concentration of a substance at a particular site within a system is continually modified by the physical processes of advection and diffusion which transport fluid constituents from location to location. However, the total amount of a substance in a closed system remains constant unless it is modified by physical, chemical, or biological processes. Employing a Fickian type expression for turbulent mass flux, the three-dimensional advection-diffusion (mass balance) equation can be written as:

$$\frac{\partial s}{\partial t} + \frac{u\partial s}{\partial x} + \frac{v\partial s}{\partial y} + \frac{w\partial s}{\partial z} - \frac{\partial}{\partial x}\left(K_x \frac{\partial s}{\partial x}\right) - \frac{\partial}{\partial y}\left(K_y \frac{\partial s}{\partial y}\right) - \frac{\partial}{\partial z}\left(K_z \frac{\partial s}{\partial z}\right) = \Sigma S \qquad (2\text{-}5)$$

where s = concentration of constituent

u = velocity in x-direction

v = velocity in y-direction

w = velocity in z-direction

K_x, K_y, K_z = eddy diffusion coefficients

ΣS = sum of source/sink rates

t = time

Difficulties exist in trying to correctly quantify the terms in this equation. The unsteady velocity field (u,v,w) must be evaluated separately from equation (2-5) so that the pollutant concentration, s, can be prescribed. Even then, the solution to the three-dimensional system representation is difficult to obtain. Hence simplified versions of equation (2-5) are used instead.

2.3.1.1 Vertical Advective Transport

The basic vertical transport mechanisms include the following: 1) water flow in the direction of the velocity field (advection), 2) dispersion by diffusional processes, 3) buoyant forces, and 4) settling of particulates.

A coarse representation of the water system as a CSTR is often sufficient for problem applications to some lakes where detailed hydrodynamics are not required. Since in this zero-dimensional type of representation there is only a single element, no transport direction can be specified. The quantity of flow entering and leaving the system alone determines water volume changes within the element.

For lake systems with long residence times and stratification in the vertical direction, one-dimensional representations are common (see Section 2.2.1). Horizontal layers are imposed and advective transport is assumed to occur only in the vertical direction. The basic vertical advection/diffusion transport equation typically used in conjunction with this system representation is:

$$\frac{\partial C}{\partial t} = \frac{-Q_v}{A} \frac{\partial C}{\partial z} + D_z \frac{\partial^2 C}{\partial z^2} + \frac{1}{A \Delta z} (Q_{h,i} C_i - Q_{h,o} C) \Sigma \pm S \qquad (2\text{-}6)$$

where C = concentration of specific constituent

C_i = concentration of constituent in upstream flow

D_z = effective diffusion coefficient

A = horizontal surface area of hydraulic element

Q_v = vertical flow through element (layer)

$Q_{h,i} Q_{h,o}$ = horizontal inflow and outflow to element, respectively

Δz = element thickness

S = source/sink rates

The first term on the right-hand side of the equation represents advective vertical transport, the second term represents diffusional transport based on a concentration gradient, the third term represents the horizontal inflow-outflow, and the fourth term (the source/sink term) represents the rate of internal production or consumption of the constituent C.

Generally the tributary inflows and outflows are assumed to enter and leave the lake at water levels of equal density. Since water is essentially incompressible the inflow is assumed to generate advective flow between all elements above the level of entry. The elements below this level, containing higher density water, are assumed to be unaffected. A simplified diagram of this type of lake representation, which illustrates the physical transport processes, is shown in Figure 2-5.

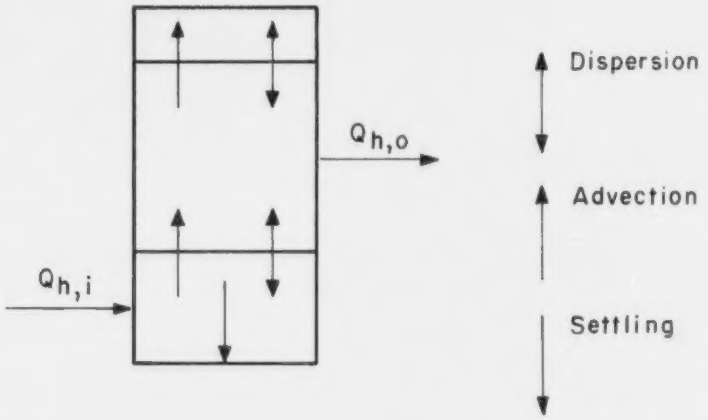

Figure 2-5. One-dimensional, advective-dispersive vertical transport.

The source/sink term of a mass balance expression generally includes settling, often of significance in vertical mass transport in lakes. Mixing and turbulence associated with fresh water flow in rivers and tidal action in estuaries are frequently of significant magnitude to minimize the settling effect in riverine and estuarine systems (O'Connor, et al., 1975). Specific settling formulations and values are discussed elsewhere in this report under specific constituent source/sink expressions.

A two-dimensional estuarine model having vertical and longitudinal spatial differentiation is another type of representation which requires a vertical transport formulation. A simplified representation illustrating the transport mechanisms is shown in Figure 2-6.

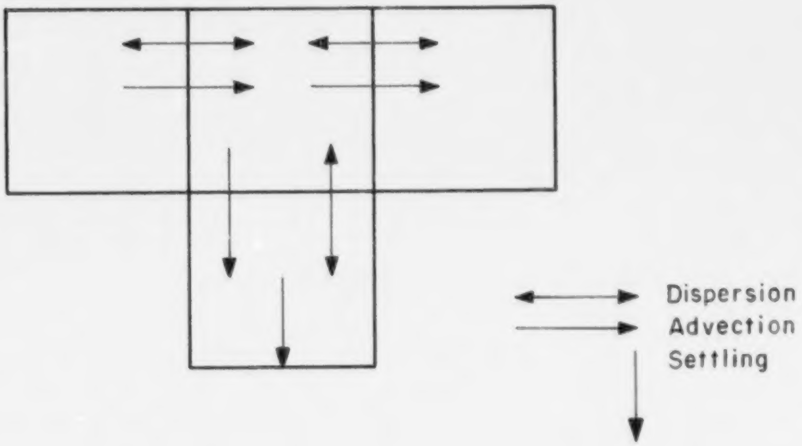

Figure 2-6. Two-dimensional, advective-diffusive transport in the longitudinal and vertical directions.

In this particular representation, the advection and diffusion processes are variable in space in the longitudinal direction as well as in the vertical. Generally, if vertical differentiation is necessary in a given model application, settling effects will also be significant.

Three-dimensional system representations, incorporating vertical, lateral, and longitudinal transport, are rarely employed. The use of three spatial dimensions introduces substantial additional complexity over one- and two-dimensional representations. The larger computing facilities needed for a complete spatial description often severely limits the amount of biological and chemical detail which can be built into a model. Frequently, therefore, prototype systems are often represented with the velocity and concentration field averaged over at least one spatial dimension.

In Tetra Tech's (1975) three-dimensional model of Lake Ontario, the wind stress generates advective flow from one element to the next in the horizontal direction. Horizontal transport is expressed in terms of a stream function. Once the horizontal velocities through an element are established, vertical transport is addressed on a basis of continuity.

2.3.1.2 Horizontal Advective Transport

All stream models reviewed represent stream systems conceptually as horizontal, linear networks of segments or volume elements. The process of advection is assumed to transport a constituent horizontally by movement of the parcel of water containing the constituent.

The simplest situation encountered is that of a one-dimensional flowing stream or river where the dispersion of mass is neglected because of its small magnitude relative to the flow. In this case, advection is the major transport mechanism. This simplification is important in terms of computational complexity and the amount of information required. The fundamental equation that governs the transport of material in this type of non-dispersive system is:

$$\frac{\partial C}{\partial t} = -\frac{1}{A}\frac{\partial(QC)}{\partial x} - k_c C \qquad (2\text{-}7)$$

where C = concentration of substance

A = cross-sectional area

k_c = first-order decay coefficient

For a river with a constant flow rate and constant dispersion, the basic form of the one-dimensional equation for horizontal transport becomes:

$$\frac{\partial C}{\partial t} = -\frac{u\partial C}{\partial x} + \frac{E\partial^2 C}{\partial x^2} + \Sigma \pm S \qquad (2\text{-}8)$$

where E = dispersion coefficient (assumed constant over x)

S = source/sink rate for substance C

The term $u\partial C/\partial x$ represents the mass flux due to advection.

In horizontally layered, one-dimensional lake models, inputs and outputs of water at various depths in the geometric representation are specified. Models of this type commonly include empirical relationships for densimetric flow in the vertical direction.

Baca and Arnett (1976) have used a pseudo-two-dimensional, laterally mixed, analytical-empirical approach to characterize the complex "interflows" through a reservoir and at its spillway(s). The "interflow" is the horizontal flow between segments, and interflow depth is based on density compatibility. In this approach, the outflow history of one segment becomes the inflow regime for the next. The interflow half thickness, labeled D, is computed from Debler's criterion (U.S. Corps of Engineers, 1974):

$$D = \left(42.0 \frac{Q}{W} \frac{1}{\sqrt{-\beta}} \right)^{1/2} \qquad (2\text{-}9)$$

where D = half the thickness of the inflow or withdrawal flow field, m

Q = inflow or outflow rate, m^3/sec

W = the width of the reservoir at inflow or withdrawal depth, m

β = the density gradient at the point of inflow or withdrawal, kg/m^4 (β negative)

The U.S. Army Corps of Engineers (1974) has two different methods for distributing inflows and determining the location from which outflows arise, depending on whether or not the reservoir is stratified. For the stratified reservoir situation, Debler's criterion is used to determine the flow field thickness, similar to the approach reported by Baca and Arnett. Outflows arise from the elements within the region D meters above and below the centerline of the outlet.

For a partially stratified situation, the water is added to, or withdrawn from, the zone of complete mixing. The maximum amount of flow which will remain contained in the completely-mixed zone without encroaching into the stratified zone is determined using Craya's theory. This maximum flow, labeled "Craya's critical flow" is defined by:

$$Q = CwD^{3/2} \Delta\rho^{1/2} \qquad (2\text{-}10)$$

where Q = Craya's critical flow or the maximum amount of flow which will remain contained in the zone of complete mixing, m^3/sec

C = an empirical constant, C = 0.0742 for surface outlets and C = 0.1505 for submerged outlets

w = width of reservoir at the inflow or withdrawal depth, m

D = depth of the zone of convective mixing, m

$\Delta\rho$ = maximum density difference between the zone of complete mixing and the stratified zone, kg/m^3.

If Craya's critical flow is greater than the rate of inflow or the rate of withdrawal, the inflow or withdrawal is distributed throughout the zone of complete mixing, assuming a uniform velocity distribution. Where the rate of inflow or withdrawal is greater than the maximum that can be accommodated by the zone of complete mixing, the excess is added to or withdrawn from the stratified zone using Debler's criterion. When the reservoir is unstratified and complete mixing occurs throughout the reservoir, inflows and withdrawals are distributed throughout the reservoir, assuming a uniform velocity distribution.

In an approach used by Tetra Tech (1976) for distribution of inflow and outflow, the greatest quantity of water is deposited at the center of the entry region and the remainder is distributed to the adjacent layers using a Gaussian distribution. The thickness of the withdrawal layer, d, is calculated as follows:

$$d = 2.0 \left[q\sqrt{\frac{\rho_o}{g\beta}} \right]^{1/2} \qquad (2\text{-}11)$$

where q = volumetric discharge per unit width of reservoir

ρ_o = water density at centerline of outlet

β = $\partial\rho/\partial z$, the density gradient with depth at the centerline of outlet (β positive)

g = gravitational constant

This model was used in simulating the effects of pumped storage and the introduction of water from an external source into an impoundment. It simulates the effect on the far field and does not seek to represent the near field phenomena of a thermal plume. Ambient water is taken from the reservoir and mixed with the released water at the rising zone. To satisfy continuity, downward advection is generated at the zone of entrainment, and upward advection is assumed to occur at and above the zone of deposition.

Simons (1976) employs two separate models, one for vertically homogenous and one for vertically stratified lake systems. Each of these two models provides a complete horizontal description (both lateral and longitudinal differentiation). The vertically integrated model assumes a hydrostatic, homogeneous, and incompressible body of water in the vertical direction and is generally applicable in simulations of storm surges. The stratified lake model prescribes depths and temperatures for each layer as a function of horizontal coordinates based on actual observations from a specified time period. To facilitate the transition from homogeneous to stratified dynamics, the equations for the stratified model are formulated in terms of vertically integrated flow and the velocity difference across the thermocline.

The governing equations for the vertically-mixed model are given as follows:

$$\frac{\partial\zeta}{\partial t} = -\frac{\partial U}{\partial x} - \frac{\partial V}{\partial y} \qquad (2\text{-}12)$$

$$\frac{\partial U}{\partial t} = -g\,\frac{H\partial\zeta}{\partial x} + fV + \frac{\tau_{sx}}{\rho} - \frac{\tau_{bx}}{\rho} + A\nabla^2 U \qquad (2\text{-}13)$$

$$\frac{\partial V}{\partial t} = -g\,\frac{H\partial\zeta}{\partial y} - fU + \frac{\tau_{sy}}{\rho} - \frac{\tau_{by}}{\rho} + A\nabla^2 V \qquad (2\text{-}14)$$

where H = local undisturbed depth of lake

ζ = elevation of the free surface above a specified equilibrium level

U,V = components of vertically integrated volume transport along x-axis and y-axis of coordinate system superimposed on the lake surface

f = Coriolis parameter (taken to be 10^{-4}/sec)

τ_{sx},τ_{sy} = wind stress at surface in x and y directions, respectively

τ_{bx},τ_{by} = bottom frictional stress in x and y directions, respectively

ρ = density

A = coefficient of sub-grid-scale diffusion of momentum (estimated to be $10^6 cm^2$/sec)

∇^2 = horizontal Laplace operator

The nonlinear inertial terms were removed from Equations (2-13) and (2-14) based on earlier studies (Simons and Jordan, 1971).

Equation (2-12) states that the water surface must rise where currents converge and fall where they diverge. Equations (2-13) and (2-14) represent current oscillation along the two coordinates resulting from the following forces and effects:

1) the pressure gradient experienced by the water mass below a sloping surface

2) the tendency of currents to deviate to the right of flow (northern hemisphere) under the influence of earth's rotation (Coriolis effects)

3) the force exerted by the wind acting on the water surface

4) bottom stress

5) mixing of water masses with different momenta (turbulent diffusion)

As discussed in Section 2.2.1.3, a particularly effective approach for modeling certain types of estuaries is the construction of a pseudo-two-dimensional "link-node" network. The modified tidal hydrodynamics program of Chen and Orlob (1975) solves a set of motion equations written for the links of the system and a set of continuity equations written for the nodes, both sets of equations being one-dimensional in the horizontal direction. The basic motion equation is given as:

$$\frac{\partial u}{\partial t} + \frac{u\partial u}{\partial x} + g\,\frac{\partial h}{\partial x} + gS_x = 0 \qquad (2\text{-}15)$$

where u = mean velocity in the x-direction

x = distance

g = acceleration due to gravity

h = height of water surface above a reference plane

S_x = friction gradient along x-axis

The equation of continuity is expressed by:

$$\frac{\partial h}{\partial t} + \frac{\partial q_x}{\partial x} = 0 \qquad (2\text{-}16)$$

where q_x = tidal flow per unit width along the x-axis

2.3.2 Dispersive Transport

2.3.2.1 Introduction

The major emphasis of this introduction will be to show how dispersive effects are incorporated into the equations of motion and continuity for turbulent flow situations, where these equations are simplified through either temporal or spatial averaging. If it were feasible to solve for instantaneous velocities or concentrations without simplifying the governing equations of motion, there would be no need for dispersive terms in the equations. However, since the exact equations of motion are intractable, some modifications to these equations becomes necessary, and dispersive transport terms arise.

A consequence of temporal averaging of either instantaneous velocity or concentration is to produce a smoothed velocity or concentration response curve over time. Figure 2-7 illustrates both instantaneous velocity and time-smoothed curves. The time smoothed velocity curve is not to be confused with a steady-state velocity, but instead is given by:

$$V = \bar{V} + V' \qquad (2\text{-}17)$$

where V = instantaneous velocity

$\bar{V}$ = time-smoothed velocity

V' = velocity deviation from the time-smoothed velocity

The velocity component V' is a random component of velocity which vanishes when averaged over time (i.e., $\bar{V}' = 0$). Note that the time period of averaging can be quite short, and is small when compared to the smallest time intervals over which velocity predictions are generally made in estuaries, lakes, or streams. The latter time intervals typically range from minutes to days or even greater between successive predictions.

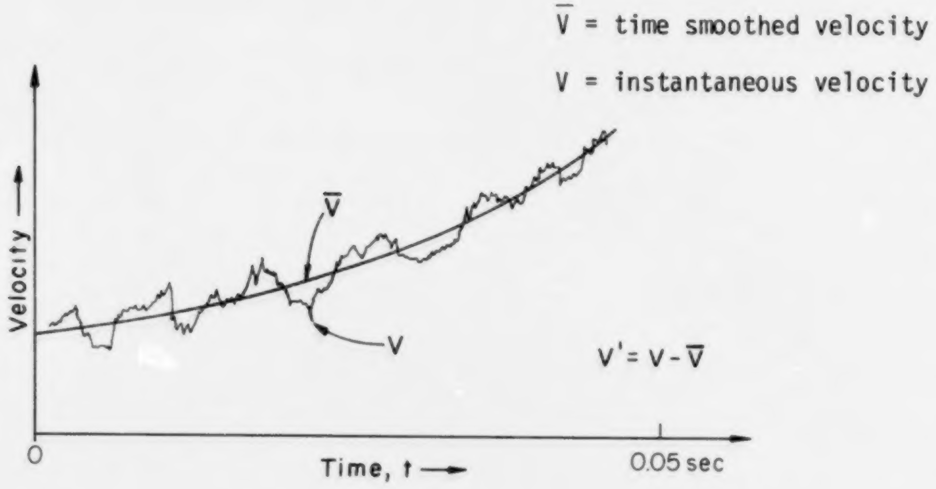

Figure 2-7. Oscillation of velocity component about a mean value (redrawn after Bird, *et al*., 1960).

By using a temporal averaging process (or performing a similar process called ensemble averaging) the stochastic component of motion is smoothed out of the momentum and continuity equations, while the deterministic component of velocity and concentration are retained. However, an additional difficulty arises in both the momentum and continuity equations. Cross-product terms result, such as $\overline{V_x'V_x'}$ and $\overline{V_x'V_y'}$ in the case of the momentum equation, and $\overline{V_x'C'}$ and $\overline{V_y'C'}$ in the case of the continuity equation (where C' is the instantaneous concentration fluctuation). These terms are not identically zero, since one term in the product is not independent of the other. In the case of the momentum equation these terms are called turbulent momentum flux terms, while in the case of the continuity equation they are called turbulent mass flux terms. It is through these terms that eddy viscosity and eddy diffusivity enter into the three-dimensional momentum and continuity equations.

In order to solve the time-smoothed equation, the time averaged cross product terms must be expressed as functions of the time averaged variables. Numerous empirical expressions have been developed to do this. The expressions most often applied are analogous to Newton's law of viscosity for turbulent momentum transport and Fick's law of diffusion for turbulent mass transfer, although no strong theoretical arguments exist for choosing these expressions. Expressed quantitatively these relationships are of the form:

$$\overline{V_x'V_y'} = -\frac{\mu^t}{\rho}\,\frac{\partial \overline{V}_x}{\partial y} \tag{2-18}$$

$$\overline{V_y'C'} = -D^t\,\frac{\partial \overline{C}}{\partial y} \tag{2-19}$$

where μ^t = eddy viscosity

D^t = eddy diffusivity

Both the eddy viscosity and diffusivity are functions of position, and hence vary in the x, y, and z directions. One might expect there to be a relationship between μ^t and D^t. Indeed, Bird, et al. (1960) has suggested the ratio of eddy viscosity to eddy diffusivity is generally in the range 0.5 to 1.0, although the extent of turbulent motion may affect this value.

In natural water bodies the values given by Equations (2-18) and (2-19) swamp their counterparts on the molecular level. Hence the Newtonian expression for momentum transport in laminar flow, and the Fickian expression for molecular diffusion may be disregarded for natural water bodies. This relationship of eddy diffusivities and molecular diffusion coefficients is depicted graphically in Figure 2-8.

The process of spatial averaging often is done over one or two dimensions. For example, vertically averaged two-dimensional momentum and mass

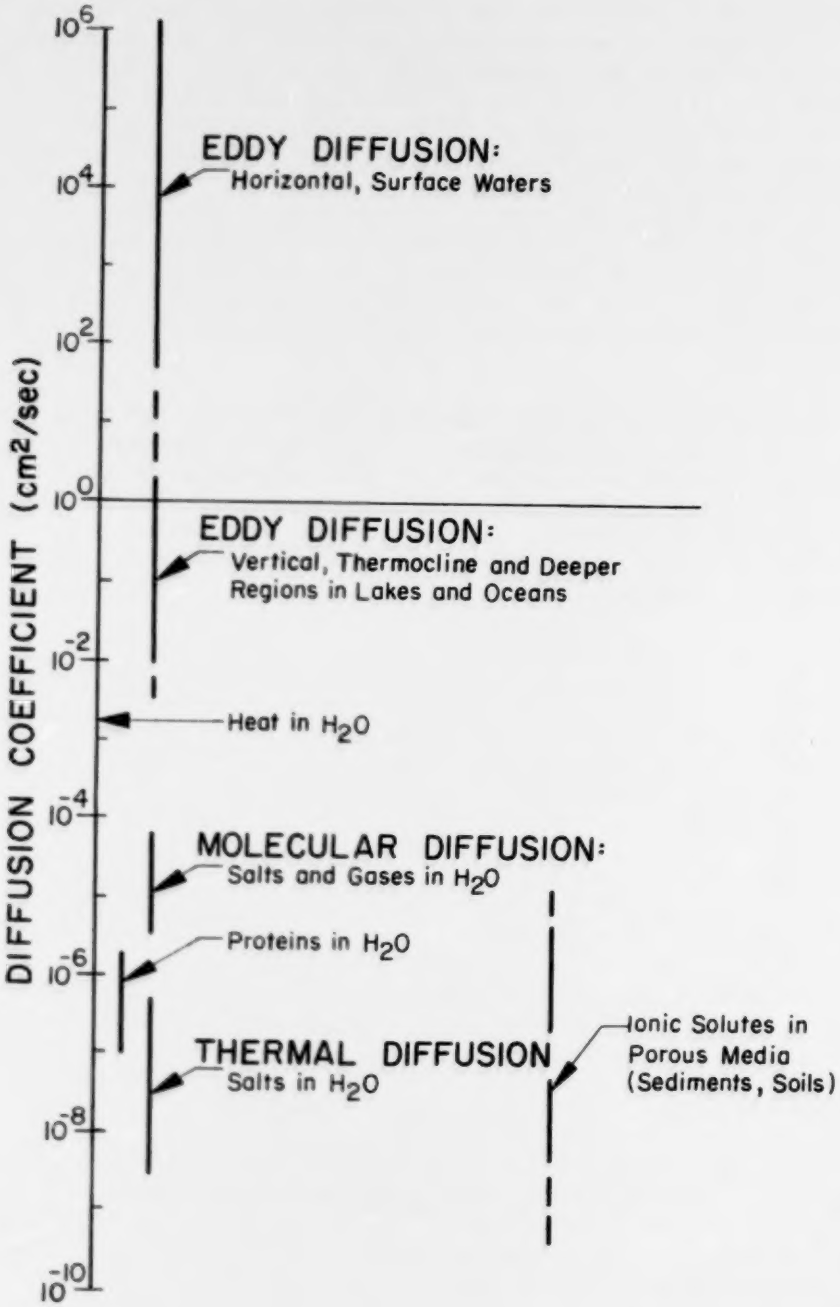

Figure 2-8. Diffusion coefficients characteristic of various environments (redrawn after Lerman, 1971).

conservation equations are often useful. The vertically averaged mass balance equation only will be discussed here for illustrative purposes. For the vertically averaged case, the concentration is expressed by a vertically averaged term and a deviation term:

$$C = C_h + C_h' \tag{2-20}$$

where C = concentration of constituent at a single point in space (as appears in the three-dimensional mass conservation equation)

C_h = vertically averaged concentration

C_h' = deviation from C_h at any point in the water column

The vertically averaged concentration term is given as the integral of C over depth:

$$C_h = \frac{1}{h}\int_0^h C dz \tag{2-21}$$

where h = water depth

z = vertical coordinate

When this integration process is performed on the three-dimensional mass conservation equation, cross product terms appear in the resulting equation, just as they do when temporal averaging is done in the three-dimensional case. These terms are produced because vertical gradients generally exist in both the concentration and velocity fields. As was done in the three-dimensional case, the cross product terms can be replaced by Fickian-type diffusion terms. The resulting "effective" diffusion coefficients, as they are sometimes called, can be expected to differ considerably from those appearing in the three-dimensional equations.

By continuing the process of spatial averaging, one-dimensional mass continuity equations can be obtained. These equations express changes only along the main flow axis, termed the longitudinal direction. The diffusion term appearing in the one-dimensional mass transport equation is the sum of two components. The first term is an integral involving the cross product of the longitudinal velocity and concentration deviations and represents the mass transport associated with the nonuniform velocity distribution. The second term is a derivative involving the spatial mean value of the three-dimensional eddy diffusivity. The integral component is represented by a Fickian expression, and the sum of the two diffusive effects is termed longitudinal dispersion.

It is important to understand that although a specified water body at a given instant has a particular degree and pattern of turbulence, the method by which that water body is modeled will dictate the type and magnitude of the diffusion term appearing in the simulation equations. Thus, a one-dimensional model uses different diffusion terms than does a three-dimensional model of the same system.

2.3.2.2 Vertical Dispersive Transport

In a lake environment, dispersion is generally caused by a different type of diffusional phenomenon than those predominant in a river or estuary system. Whereas turbulent diffusion resulting from shear stresses and irregular channel configuration and dispersion due to tidal mixing are often the principal mechanisms affecting dispersion in the latter system types, eddy diffusivity caused by wind action on the surface waters is often the primary mechanism controlling dispersion in lakes. The wind action creates eddies on the water surface and the dispersive effects are then transmitted to the deeper layers by the action of shear stresses.

Tetra Tech (1975) has used the following empirical expression for computation of the vertical eddy thermal diffusivity, K_v, in their three-dimensional hydrodynamic simulation model of Lake Ontario:

$$K_v = 100 \frac{|\vec{\tau}_w|}{\rho_o} \left(\frac{1}{1 + 3.3R_i} \right)^{1/2} \qquad (2\text{-}22)$$

where $\vec{\tau}_w$ = wind stress

ρ_o = density of fresh water at 4°C

R_i = Richardson number

In this model eddy conductivity was ignored in the horizontal plane, being assumed small in comparison to the advective effects.

Lake systems that are represented geometrically as a series of completely mixed horizontal slices consider advective and dispersive transport processes to occur in the vertical direction alone. Baca and Arnett (1976), in their one-dimensional hydrothermal lake model, proposed the following expression for determining the one-dimensional vertical dispersion coefficient:

$$D_v = a_1 + a_2 V_w d^{-4.6z/d} \qquad (2\text{-}23)$$

where D_v = vertical dispersion coefficient, m^2/sec

z = depth, m

V_w = wind speed, m/sec

d = depth of thermocline, m

a_1, a_2 = empirical constants, m^2/sec and m respectively

The following table of values (Table 2-1) for a_1 and a_2, as given by Baca and Arnett (1976), were obtained from previous model applications.

TABLE 2-1. VALUES FOR EMPIRICAL COEFFICIENTS a_1 AND a_2

Lake	Description	Max. Depth (m)	a_1 (m^2/sec)	a_2 (m)
American Falls	well-mixed	18	1×10^{-5}	1×10^{-4}
Lake Washington	stratified	65	1×10^{-6}	1×10^{-5}
Lake Mendota	stratified	24	5×10^{-7}	5×10^{-5}
Lake Wingra	well-mixed	5	5×10^{-5}	2×10^{-4}
Long Lake	linearly stratified	54	5×10^{-6}	5×10^{-5}

For reservoir systems, the U.S. Army Corps of Engineers (1974) computes the effective vertical diffusion rate between elements as a function of the density gradient. This is done in a manner similar to that in the Lake Ontario model (Tetra Tech, 1975). When the density gradient is less than the critical, as required for stability between layers, the effective diffusion coefficient is assumed constant. Mathematically, this is stated as follows:

$$D_v = A_1 \quad \text{when } \frac{\partial\rho}{\partial z\rho} \leq E_{crit} \tag{2-24}$$

$$D_v = A_2 E^{A_3} \quad \text{when } \frac{\partial\rho}{\partial z\rho} > E_{crit} \tag{2-25}$$

where D_v = effective diffusion coefficient, m^2/sec

A_1 = maximum diffusion rate, m^2/sec: $0.1 \times 10^{-4} < A_1 < 2.5 \times 10^{-4}$

A_2, A_3 = empirical constants

E = density gradient, m^{-1}

E_{crit} = density gradient at which D_C attains its maximum value (critical stability), 1/m

These relationships are shown graphically in Figure 2-9 (Water Resources Engineers, 1969).

Lick, et al. (1976) applied a three-dimensional water quality model to Lake Michigan in order to simulate the dispersion of heat in the discharge from the Point Beach Power Plant. They assumed that the vertical eddy viscosity and eddy thermal conductivity were identical with vertical eddy diffusivity. The specific relationship they used was:

$$D_v = 50 - 200 \frac{\partial T}{\partial z} \qquad (2\text{-}26)$$

where D_v = vertical eddy diffusivity, cm^2/sec

T = water temperature, °C, at depth z, m

z = depth, m

Thomann, et al. (1975) have used time- and space-varying vertical diffusivities in modeling studies for Lake Ontario. They varied the vertical diffusivity on a yearly basis, and also accounted for spatial differences between the main lake and near-shore regions. Figure 2-10 shows these relationships. Murphy, during the International Field Year for the Great Lakes, as reported by Thomann, et al. (1975), found that values of the vertical diffusivity coefficient generally ranged from 0.1 cm^2/sec to 22 cm^2/sec, depending on effects such as wind conditions and density stratification.

2.3.2.3 Horizontal Eddy Diffusive Transport

Generally, horizontal eddy diffusivity is several orders of magnitude greater than the vertical eddy diffusivity. The Journal of the Fisheries Research Board of Canada (Lam and Jacquet, 1976) reported a range of values for the horizontal diffusivity in lakes from 10^4 to 10^6 cm^2/sec. Thomann, et al. (1975) used a horizontal diffusivity of 9,000 cm^2/sec for most parts of Lake Ontario. However, the horizontal coefficients were set to zero for the stratification period to simulate the thermal bar effect which produces a restriction of the mixing of near-shore waters with main lake waters (see Figure 2-11).

Lam and Jacquet (1976) obtained Equation (2-27) for the horizontal eddy diffusivity for lakes, D_h (Cm^2/sec), based on experimental results:

$$D_h = .0056L^{1.3} \qquad (2\text{-}27)$$

where L = length scale of grid, cm

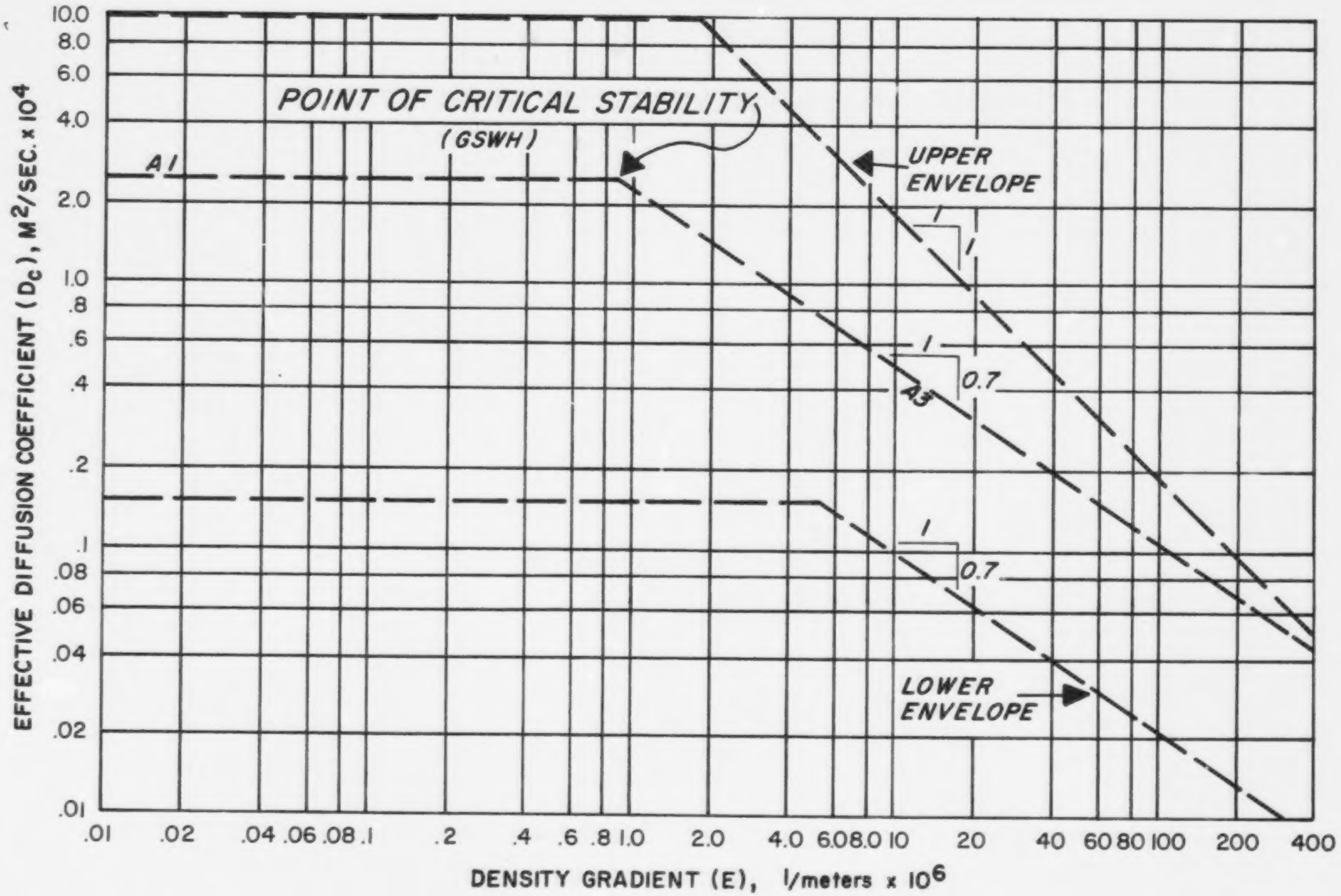

Figure 2-9. Log of effective diffusion versus log of density gradient (Water Resources Engineers, 1969).

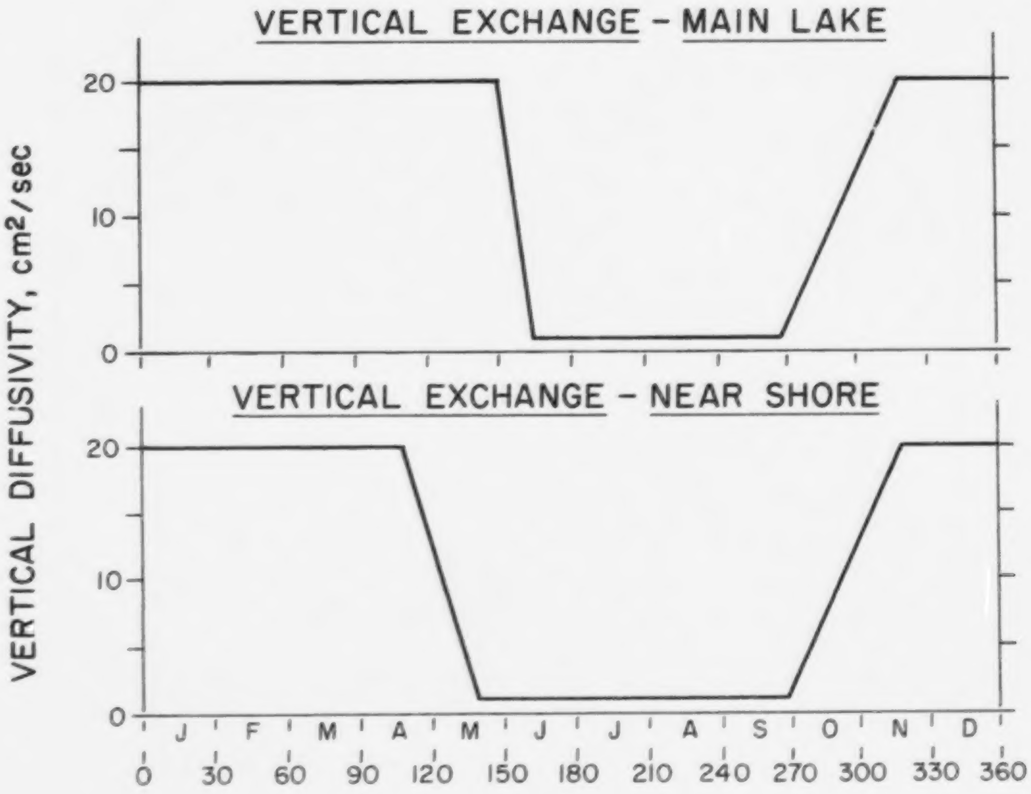

Figure 2-10. Assumed vertical dispersion coefficients for three-dimensional model (after Thomann, et al., 1975).

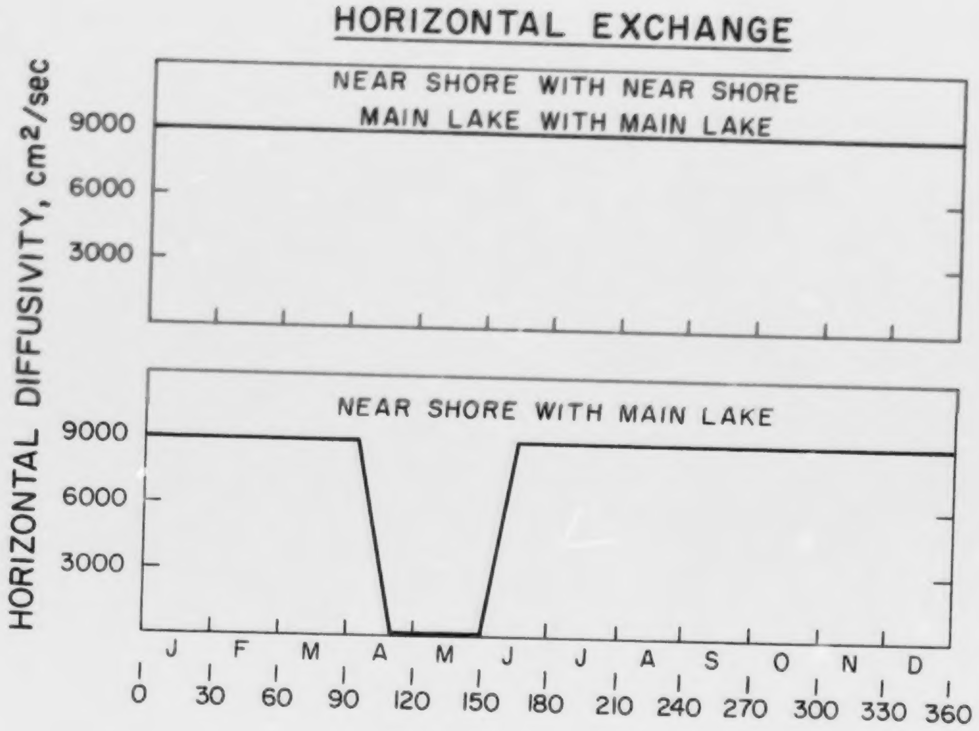

Figure 2-11. Horizontal diffusivities used in Lake Ontario modeling studies, illustrating the "thermal bar effect" (after Thomann, et al., 1975).

For a grid size larger than 20 km, the diffusivity is expected to be essentially constant (10^6 cm^2/sec).

2.3.2.4 Longitudinal Dispersion

As previously discussed in Section 2.3.2.1, longitudinal dispersion is the "effective diffusion" that occurs in one-dimensional mass transfer equations that have been integrated over the cross sectional area perpendicular to flow. This one-dimensional approach to modeling has often been applied to tidal and nontidal rivers, and to some estuaries. Dispersion in estuaries and tidal rivers will be discussed first, in this section, followed by a brief discussion of dispersion in streams.

The magnitude of the one-dimensional dispersion coefficient in estuaries and tidal rivers is determined in part by the time scale for which the simulation is performed. The time scale specifies the interval over which quantities that generally change instantaneously, such as tidal current, are averaged. For shorter time scales the simulated hydrodynamics and water quality relationships are more accurately resolved and hence, in such models, smaller dispersion coefficients are needed than in those which, for example, have hydrodynamics averaged over a tidal cycle.

The magnitude of the dispersion coefficient can also be expected to change as a function of location within an estuary. Since the one-dimensional dispersion coefficient is the result of spatial averaging over a cross section perpendicular to flow, the greater the deviation between actual velocity and the area-averaged velocity, and between actual constituent concentrations and area-averaged concentrations, the larger will be the dispersion coefficient. These deviations are usually largest near the mouths of estuaries due to density gradients set up by the interface between fresh and saline water. Strong tidal currents may also result in large dispersion coefficients.

Because of the time scale and location dependency of the dispersion coefficient, it is convenient to divide the discussion of dispersion into real time and tidally averaged time expressions, and then to subdivide these according to estuarine location, i.e., the salinity intrusion region and the freshwater tidal region. The salinity intrusion region is that portion of the estuary where a longitudinal salinity gradient exists. The location of the line of demarcation between the salinity intrusion region and the freshwater tidal region varies throughout the tidal cycle, and also depends on the volume of freshwater discharge. It should also be noted that the freshwater tidal region can contain saline water, if the water is of uniform density throughout the region (TRACOR, 1971). There is at present no analytical method for predicting dispersion in the salinity intrusion region of estuaries. However, because of the presence of a conservative constituent (salinity), empirical measurements are easily performed. In the freshwater tidal region, analytical expressions have been developed, while empirical measurements become more difficult due to the lack of a naturally occurring conservative tracer.

For real time simulations in the constant density region of estuaries and tidal rivers, the following expression has been proposed (TRACOR, 1971):

$$E_L = 100\ n\ U_{max}\ R_H^{5/6} \qquad (2\text{-}28)$$

where E_L = longitudinal dispersion coefficient in the constant density region, ft^2/sec

n = Manning's roughness coefficient, $ft^{1/6}$

U_{max} = maximum tidal velocity, ft/sec

R_H = hydraulic radius, ft

Feigner and Harris (1970) used the following empirical expression to represent real time longitudinal dispersion for the constant density region in their estuary water quality model:

$$E_L = C_1\ E^{1/3} L_e^{4/3} \qquad (2\text{-}29)$$

where E_L = longitudinal dispersion coefficient, $length^2/time$

E = rate of energy dissipation per unit mass

L_e = mean size of eddies participating in the mixing process

C_1 = function of relative channel roughness

For computational purposes, Feigner used the following simplification:

$$E_L = 0.042\ |u| R \qquad (2\text{-}30)$$

where R = hydraulic radius, ft

$|u|$ = absolute value of velocity, ft/sec

The determination of real time dispersion coefficients in the salinity intrusion region requires field data on salinity distribution. Once the field data have been collected, the magnitudes of the dispersion coefficients are found by fitting the solution of the salinity mass transfer equation to the observed data. As reported in TRACOR (1971), this technique has been applied to the Rotterdam Waterway, an estuary of almost uniform depth and width. The longitudinal dispersion coefficient was found to be a function of x, the distance measured from the mouth (ft), as follows:

$$E_L = 13000\left(1 - \frac{x}{L}\right)^3 \qquad (2\text{-}31)$$

where E_L = real time longitudinal dispersion coefficient in salinity intrusion region, ft^2/sec

L = length of entire tidal region of the estuary

At the estuary mouth, E_L was found to be 13,000 ft^2/sec or 40 mi^2/day by using the technique described above. Under the same conditions in a constant density region, Equation (2-28) would predict an E_L of 175 ft^2/sec or 0.5 mi^2/day. This illustrates the large difference that can be expected between the real time dispersion coefficient in the salinity intrusion region of an estuary and the constant density region.

For tidally averaged or net nontidal flow simulations, since the system hydrodynamics are averaged over a tidal period or longer, the dispersion coefficient must include the additional effects of tidal mixing, which do not need to be included for real time simulations. No general analytical expressions exist for this coefficient. Hence, values must be determined based on observed data, or based on empirical equations having parameters that are determined from observed data. This limitation exists for both the constant density and salinity intrusion regions of the estuary.

In their one-dimensional tidally averaged estuary model, Johanson, et al. (1977) used an empirical expression, comprised of three principal components (tidal mixing, salinity gradient, and net freshwater advective flow) for the dispersion coefficient. The relative location in an estuary where each of these factors is significant, and their relative magnitudes, are shown in Figure 2-12.

The expression used by Tetra Tech is:

$$E_L = C_1\left(|\bar{u}| + \sigma_u\right)\left(\bar{y} + \sigma_y\right) + C_4\left(\frac{\Delta S}{\Delta x}\right) \qquad (2\text{-}32)$$

where E_L = tidally averaged dispersion coefficient, ft^2/sec

C_1 = tidally-induced mixing coefficient (dimensionless)

$\bar{y}$ = tidally averaged depth, ft

$|\bar{u}|$ = tidally averaged absolute value of velocity, ft/sec

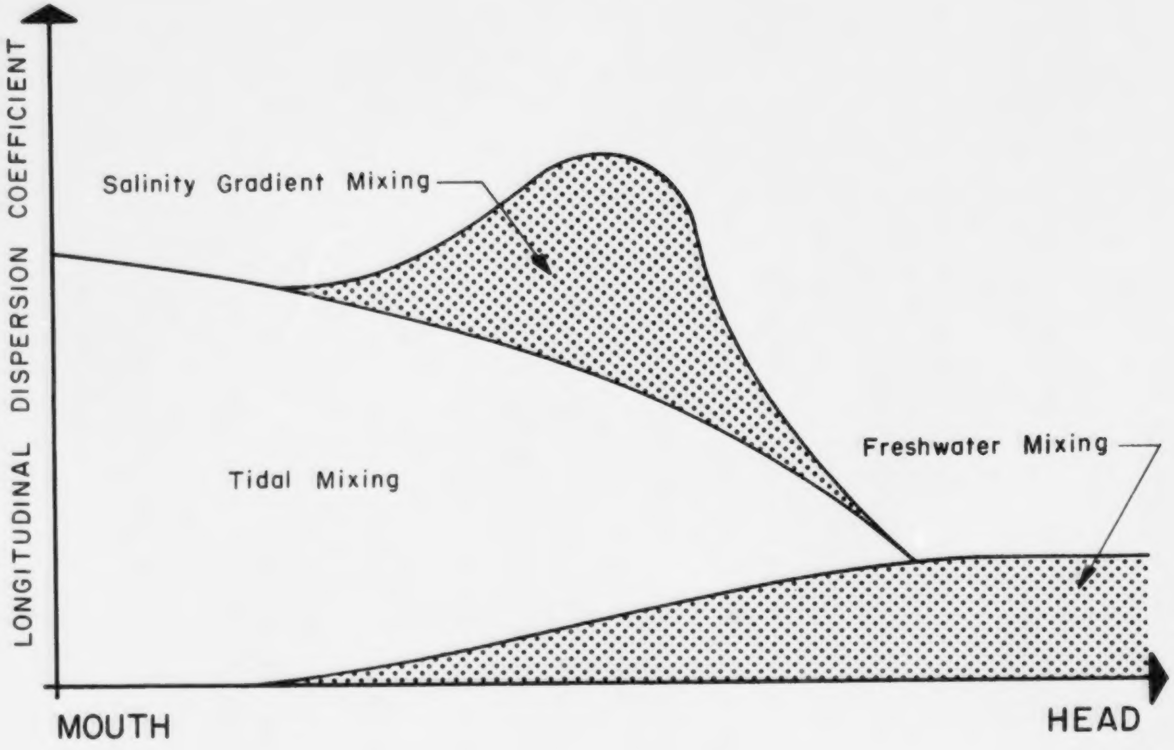

Figure 2-12. Factors contributing to tidally averaged dispersion coefficients in the estuarine environment (modified after Zison, et al., 1977).

σ_u = standard deviation of velocity, ft/sec

σ_y = standard deviation of depth, ft

C_4 = density-induced mixing coefficient, ft^3/sec/mg/l-salinity

$\frac{\Delta S}{\Delta x}$ = salinity gradient, mg/l/ft

The first term on the right side of Equation (2-32) represents mixing brought about by the oscillatory flows associated with the ebbing and flooding of the tide. The second term represents additional mixing when longitudinal salinity gradients are present.

One common method of experimentally determining the tidally averaged dispersion coefficient is by the "fraction of freshwater method," as explained by Officer (1976). The expression is:

$$K_L = \frac{Rs}{A(ds/dx)} = \frac{R(f-1)}{A(df/dx)} \qquad (2\text{-}33)$$

where K_L = tidally averaged dispersion coefficient, ft^2/sec

s = mean salinity at a particular location averaged over depth, mg/l

A = cross-sectional area normal to flow, ft^2

R = total river runoff flow rate, cfs

f = freshwater fraction = $\frac{\sigma - s}{\sigma}$, unitless

σ = normal ocean salinity of the coastal water into which the estuary empties, mg/l

x = distance along estuary axis, ft

K_L can be calculated at any location within the estuary if the river flow, cross-sectional area, and salinity or freshwater fraction distributions are known.

Hydroscience (1971) has collected values of tidally averaged dispersion coefficients for numerous estuaries, and these values are shown in Table 2-2. Some additional information for these and other estuaries will be given in Table 3-6.

In his book, Officer (1976) reviews studies performed in a number of estuaries throughout the world. He discusses the dispersion coefficients which have been determined, and a summary of values for these estuaries is contained in Table 2-3. Many values were developed using the fraction of freshwater method just discussed.

TABLE 2-2. TIDALLY AVERAGED DISPERSION COEFFICIENTS FOR SELECTED ESTUARIES (FROM HYDROSCIENCE, 1971)

Estuary	Freshwater Inflow (cfs)	Low Flow Net Nontidal Velocity (fps) Head - Mouth	Dispersion Coefficient (mi²/day*)
Delaware River	2,500	0.12-0.009	5
Hudson River (N.Y.)	5,000	0.037	20
East River (N.Y.)	0	0.0	10
Cooper River (S.C.)	10,000	0.25	30
Savannah R. (Ga., S.C.)	7,000	0.7-0.17	10-20
Lower Raritan R. (N.J.)	150	0.047-0.029	5
South River (N.J.)	23	0.01	5
Houston Ship Channel (Texas)	900	0.05	27
Cape Fear River (N.C.)	1,000	0.48-0.03	2-10
Potomac River (Va.)	550	0.006-0.0003	1-10
Compton Creek (N.J.)	10	0.01-0.013	1
Wappinger and Fishkill Creek (N.Y.)	2	0.004-0.001	0.5-1

*1 mi^2/day = 322.67 ft^2/sec

TABLE 2-3. TIDALLY AVERAGED DISPERSION COEFFICIENTS (FROM OFFICER, 1976)

Estuary	Dispersion Coefficient Range (ft^2/sec)	Comments
San Francisco Bay		Measurements were made at slack water over a period of one to a few days. The fraction of freshwater method was used. Measurements were taken over three tidal cycles at 25 locations.
Southern Arm	200-2,000	
Northern Arm	500-20,000	
Hudson River	4,800-16,000	The dispersion coefficient was derived by assuming K_L to be constant for the reach studied, and that it varied only with flow. A good relationship resulted between K_L and flow, substantiating the assumption.
Narrows of Mercey	1,430-4,000	The fraction of freshwater method was used by taking mean values of salinity over a tidal cycle at different cross sections.
Potomac River	65-650	The dispersion coefficient was found to be a function of distance below the Chain Bridge. Both salinity distribution studies (using the fraction of freshwater method) and dye release studies were used to determine K_L.
Severn Estuary	75-750 (by Stommel) 580-1,870 (Bowden)	Bowden recalculated K_L values originally determined by Stommel, who had used the fraction of freshwater method. Bowden included the freshwater inflows from tributaries, which produced the larger estimates of K_L.

(continued)

TABLE 2-3 (continued)

Estuary	Dispersion Coefficient Range (ft^2/sec)	Comments
Tay Estuary	530-1,600 (up estuary) 1,600-7,500 (down estuary)	The fraction of freshwater method was used. At a given location, K_L was found to vary with freshwater inflow rate.
Thames Estuary	600-1,000 (low flow) 3,600 (high flow)	Calculations were performed using the fraction of freshwater method, between 10 and 30 miles below London Bridge.
Yaquina Estuary	650-9,200 (high flow) 140-1,060 (low flow)	The dispersion coefficients for high flow conditions were substantially higher than for low flow conditions, at the same locations. The fraction of freshwater method was used.

In streams, one of the more popular equations for estimating dispersion is the Elder equation, which is given as:

$$E_L = 22.6\ n\ \bar{u}\ D^{0.833} \tag{2-34}$$

where n = Manning's coefficient, $ft^{1/6}$

$\bar{u}$ = mean velocity, ft/sec

D = depth of flow, ft

E_L = longitudinal dispersion coefficient, ft^2/sec

Bansal (1976), however, suggests that the longitudinal dispersion rates predicted using the above formulation tend to be low, resulting in higher concentrations of shorter duration than when better estimates of the dispersion coefficients are used. He offers the following alternative expression for computing the longitudinal dispersion coefficient, based on the Reynold's number for flow and the channel configuration of the stream:

$$\log K \frac{\bar{u}}{v} \frac{E_L}{vH} = 6.45 - 0.762 \log \left(\frac{\rho v H}{\mu} \right) \tag{2-35}$$

where E_L = longitudinal turbulent diffusion coefficient, ft^2/sec

K = regional dispersion factor (equal to 1 for Big Blue River), unitless

$\bar{u}$ = average velocity (Q/A), ft/sec

v = x/t_p where x = reach length and t_p = time to peak arrival of constituent concentration at sampling station, ft/sec

H = $\frac{A}{B}$ where A = cross-sectional area and B = top width of flow, ft

ρ = density, lb/ft^3

μ = coefficient of viscosity, $lb\text{-}sec/ft^2$

Using this alternative expression, Bansal reported considerably higher values for the longitudinal dispersion coefficient than obtained with the same conditions on the Big Blue River using the Elder expression. Bansal's values ranged from 28.6 to 380.7 ft^2/sec, where previously they had been 0.91 to 2.29 ft^2/sec using the Elder expression.

Gloyna, et al. (1971) also calculated longitudinal dispersion coefficients for stream velocities ranging from 0.33 to 3.30 ft/min using time-concentration curves from Rhodamine-B dye studies. The dispersion coefficients were found to be representable by an empirical relationship of the form:

$$D_L = 3.26\ u^{0.607} \qquad (2\text{-}36)$$

where u = average velocity in ft/min

D_L = longitudinal dispersion coefficient, ft^2/min

Battelle (1974), in their Gray's Harbor/Chehalis River application, assumed diffusion to be negligible because "of the nebulous nature of hydrodynamic dispersion coefficients." These investigators further contend that finite-difference solutions to advection-diffusion equations introduce "pseudo-dispersion effects" which can completely mask the actual solution. Hydroscience (1971) has also suggested disregarding longitudinal dispersion in streams upstream of tidal influence, for simplified applications.

2.3.2.5 Tidal Exchange

The hydrodynamic behavior of an estuary is controlled primarily by tides at the mouth, although at times of high runoff, tributary flows may dominate. During a tidal day (about 25 hours) normally two high and two low tides occur. However, because of the complexity of tidal patterns, diurnal tides (occurring once daily) and mixed tides (varying between once and twice daily) can occur.

During flood tide, ocean water moves into the system and estuarial water is pushed inland and mixed with fresh water entering through the landward boundary. The ebbing tide is characterized by a reversal of flow and a discharge of the freshwater-ocean water mixture through the seaward boundary to the ocean. Some fraction of estuarial water is lost to the ocean. The remainder mixes with new ocean water and returns to the estuary on the succeeding flood.

The transition between flood and ebb conditions is called "slack water" or "slack tide"; it occurs at different times throughout the system depending on the velocity of propagation of the tidal wave from the mouth of the estuary. Since tidal motions are dominated by the moon, a complete tidal cycle has a period of approximately 25 hours, a lunar day. Variations in amplitude and phase of the tide are associated with the combined effects of the sun and the moon from month to month over the year.

Generally, in the modeling of estuarine systems, tidal information is necessary to provide an indication of the amount of energy available for mixing (being proportional to the square of the tidal range), and to determine the amount of water available for dilution. In addition, the excursion of pollutants depends on the range and duration of ebb and flood tides. The tidal heights or currents are often required, therefore, as natural boundary conditions.

The primary purpose of a mathematical tidal hydrodynamics model, accordingly, is to provide quantitative temporal descriptions of tidal flows, current velocities, water levels, and tidal volumes. Prediction of tidal heights by harmonic analysis is well-established, with discrepancies from predicted heights occurring due to storm surges and freshets from local precipitation (Callaway, 1971). In the absence of desired tidal data, predictions in the Coast and Geodetic Survey Tide Tables (now published by the National Oceanic and Atmospheric Administration) for the tidal elevations at the four extreme stages of the tide can be used along with the time of occurrences (Feigner and Harris, 1970). After the tidal elevations have been referenced to the model datum, a harmonic regression (or Fourier analysis) can then be performed.

Tidal current prediction is reportedly less well behaved from the viewpoint of predictability than are heights (Callaway, 1971). Tidal currents are composed primarily of a transitory component associated with the mean hydrologic flux and an oscillatory component induced by an imposed tide at the estuarine boundary. In addition, there may be components of the current attributed to wind stress, density differences, local runoff and the effect of the earth's rotation. Of the secondary effects, wind stress is usually of interest in shallow, well-mixed estuaries like San Francisco Bay and should be considered in special cases.

Chen and Orlob (1975) have adopted a simple and stable method for representing tidal fluctuations. The method is based on the following assumptions:

1. The first increment of ebbing water at the estuary mouth is considered lost to sea.
2. The last increment of ebbing water before a tide reversal at the estuary mouth returns to the estuarine system with no change in quality; i.e., the first increment entering on the flooding tide is equivalent to the last leaving on the preceding tide (boundary condition no. 1).
3. The last increment of water to enter a system on a flooding tide is equivalent in quality to raw sea water (boundary condition no. 2).
4. Water entering the system between the beginning and end of the flood tide may be described by interpolating linearly between the two bounds according to time of entry.

Based on this procedure, one need only specify the quality of sea water to compute tidal exchange.

2.3.3 Heat Budgets

The transfer of energy which occurs at the air-water interface is generally handled in one of two ways in river, lake, and estuary models. A simplified approach is to input temperature values directly and avoid a more complete formulation of the energy transfer phenomena. This approach is most often applied to those aquatic systems where the temperature regime is easily described. Alternatively, the various energy transfer phenomena which occur at the air-water interface can be considered in a heat budget formulation.

In a complete atmospheric heat budget formulation, three mechanisms are generally considered: radiation (solar and atmospheric), evaporation, and convection. Typically, the combined influence of these mechanisms is represented by a net external heat exchange (flux) term, H. This term may, in some instances, be input to the model as a specified value (Lick, et al., 1976; Tetra Tech, 1975), but the importance of time and spatial variations should be considered carefully before so doing.

Lombardo (1973) defines the heat exchange across the air-water interface, H, with the following empirical expression:

$$H = S_i - \left(60 + 6.2\ T_w - 5.4\ T_a\right) - 1634E - 0.89u\left(T_w - T_a\right) \qquad (2\text{-}37)$$

where S_i = incident solar radiation

T_a = air temperature, °F

T_w = water temperature, °F

u = wind velocity, mph

E = evaporation, in/hr = $0.000073u\ (\rho_w - \rho_a)$

ρ_w = the vapor pressure for water in mb

ρ_a = the vapor pressure for air in mb

The net external heat flux, H, is also often formulated as an algebraic sum of several component energy fluxes in some models (e.g., Baca and Arnett, 1976; U.S. Army Corps of Engineers, 1974; Thomann, et al., 1975). A typical expression is given as (all units are Kcal/m^2-hr):

$$H = Q_s - Q_{sr} + Q_a - Q_{ar} - Q_{br} - Q_e \pm Q_c \qquad (2\text{-}38)$$

where H = net surface heat flux

Q_s = shortwave radiation incident to water surface

Q_{sr} = reflected shortwave radiation

Q_a = incoming long wave radiation from the atmosphere

Q_{ar} = reflected long wave radiation

Q_{br} = back radiation emitted by the body of water

Q_e = energy utilized by evaporation

Q_c = energy convected to or from the body of water at the surface

These flux components can be calculated within the models from semi-theoretical relations, empirical equations, and basic meteorological data. Depending on the algebraic formulation used for the net heat flux term and the particular empirical expressions chosen for each component, all or some of the following meteorological data may be required: atmospheric pressure, cloud cover, wind speed and direction, wet and dry bulb air temperatures, dew point temperature, shortwave solar radiation, relative humidity, water temperature, latitude, and longitude.

Lombardo (1972) represents the net shortwave solar radiation, Q_{sw} (langleys/day), with the following expression:

$$Q_{sw} = (1-R)\,Q_s \tag{2-39}$$

where Q_s = shortwave radiation at the surface (langleys/day)

R = reflectivity of water = 0.03, or alternately: $R = A\alpha^B$ (A,B given below in Table 2-4)

α = sun's altitude in degrees

TABLE 2-4. VALUES FOR SHORTWAVE RADIATION COEFFICIENTS A AND B (LOMBARDO, 1972)

Cloudiness	Clear	Scattered	Broken	Overcast
A	1.18	2.20	0.95	0.35
B	-0.77	-0.97	-0.75	-0.45

Various methods are available by which solar radiation can be determined. Hydrocomp has two computerized methods available for this computation (Lombardo, 1972).

The U.S. Army Corps of Engineers (1974) considers the net shortwave solar radiation rate ($Q_s - Q_{sr}$) as a function of sun angle, cloudiness, and the level of particulates in the atmosphere. Chen and Orlob, as reported by Lombardo (1973), determine the net shortwave solar radiation by considering absorption and scattering in the atmosphere.

The U.S. Army Corps of Engineers (1974), Lombardo (1972), and Chen and Orlob (1975), consider the net long wave radiation rate ($Q_a - Q_{ar}$) as a function of air temperature and cloudiness according to the following expression:

$$Q_{at} = 1.23 \times 10^{-16} \left(1 + 0.17 \cdot \text{CLOUD}^2\right)\left(T_a + 273\right)^6 \qquad (2\text{-}40)$$

where Q_{at} = net long wave atmospheric radiation, kcal/m^2/sec

CLOUD = cloud cover, fraction

T_a = dry bulb air temperature, °C

This expression assumes the reflectivity of water for atmospheric radiation is 0.03.

The Stefan-Boltzman expression is most often used to determine back radiation by the water body:

$$Q_{br} = 0.97\, \sigma\, T_w^{\ 4} \qquad (2\text{-}41)$$

where Q_{br} = long wave back radiation, cal/m^2-sec

T_w = water temperature, °K

σ = Stefan-Boltzman constant = 1.357×10^{-8}, cal/m^2-sec/°K^4

The U.S. Army Corps of Engineers (1974) uses the following linearization of Equation (2-41) to express the back radiation emitted by the water body:

$$Q_{br} = 73.6 + 1.17\, T \qquad (2\text{-}42)$$

where T = water temperature, °C

In the range of 0° to 30°C, this linear function has a maximum error of less than 2.1% relative to Equation (2-41).

Heat loss due to water evaporation, Q_e, is represented by the U.S. Army Corps of Engineers (1974), Chen and Orlob (1975), and Lombardo (1972), with the following expression:

$$Q_e = \rho L_w E \tag{2-43}$$

where Q_e = heat loss due to evaporation, kcal/m^2-sec

ρ = fluid density, kg/m^3

L_w = latent heat of vaporization, kcal/kg

E = evaporation rate, m/sec

The evaporation rate, E, is approximated by the semi-empirical function:

$$E = \left(a + bV\right)\left(e_s - e_a\right) \tag{2-44}$$

where a,b = empirical coefficients

V = wind speed over water surface, m/sec

e_s = saturation vapor pressure at the surface water temperature, mb

e_a = vapor pressure of the overlying atmosphere, mb

The empirical coefficient, a, has often been taken to be zero, while b ranges from 1×10^{-9} to 5×10^{-9}.

The value of e_s is a nonlinear function of the surface temperature. However e_s can be estimated in a piecewise linear fashion as follows:

$$e_s = \alpha_i + \beta_i T_w \tag{2-45}$$

where α_i, β_i = empirical coefficients with values as given in Table 2-5 below.

T_w = water temperature, °C

The following empirical expression (Lombardo, 1972) can be used for determining the latent heat of vaporization, L_w, in kcal/kg:

$$L_w = 597 - 0.57\, T_w \tag{2-46}$$

where T_w = water temperature, °C

TABLE 2-5. VALUES FOR EMPIRICAL COEFFICIENTS α_1 AND β_1

Temperature Range, °C	α_i	β_i
0-5	6.05	0.522
5-10	5.10	0.710
10-15	2.65	0.954
15-20	-2.04	1.265
20-25	-9.94	1.659
25-30	-22.29	2.151
30-35	-40.63	2.761
35-40	-66.90	3.511

The U.S. Army Corps of Engineers (1974) defines the convective heat transfer, Q_c, by the following relationship:

$$Q_c = R\, Q_e \qquad (2\text{-}47)$$

where R = Bowen ratio = $(6.19 \times 10^{-4})\, p\, \dfrac{T_w - T_a}{e_s - e_a}$

p = atmospheric pressure, mb

T_a = dry bulb air temperature, °C

Chen and Orlob, as reported by Lombardo (1973), consider similar variables in their formulation for convective transfer, given as:

$$Q_c = \frac{p}{0.622}\, \rho_w\, C_p\, N_c\, u \left(T_a - T_w\right) \qquad (2\text{-}48)$$

where p = local barometric pressure, mb

ρ_w = water density

C_p = specific heat of air, kcal/kg -°C

N_c = empirical constant

u = wind speed, m/sec

Similarly, convective heat exchange is given by Lombardo (1972) in kcal/m^2-hr, as:

$$\text{CONVK } p \times 10^{-4} / p_o \; u \left(T_a - T_w \right) \qquad (2\text{-}49)$$

where p = barometric pressure at the site, mb

p_o = sea level pressure, mb

CONVK = coefficient of convection, ranging from 1-20

u = wind speed, m/hr

T_a = air temperature, °C

T_w = water temperature, °C

Baca and Arnett (1976) present the following table (Table 2-6), which compares the amount of heat loss and gain by the various components:

TABLE 2-6. RANGE OF VALUES FOR VARIOUS COMPONENT HEAT FLUXES (BACA AND ARNETT, 1976)

Component	Symbol	Range of Loss or Gain (kcal/m^2-hr)
Shortwave solar radiation	Q_s	30 → 300
Reflected shortwave	Q_{sr}	5 → 25
Net shortwave	$Q_{sn} = Q_s - Q_{sr}$	25 → 375
Long wave atmospheric radiation	Q_a	225 → 360
Reflected long wave radiation	Q_{ar}	5 → 15
Net long wave radiation	$Q_{an} = Q_a - Q_{ar}$	220 → 345
Net surface radiation	Q_{br}	225 → 400
Evaporative heat loss	Q_e	25 → 900
Convective heat loss/heat gain	Q_c	-35 → 50

A similar range of values for the various component heat fluxes (originally developed by Parker and Krenkel (1970)) is given by Lombardo (1972) (Table 2-7):

TABLE 2-7. RANGE OF VALUES FOR VARIOUS COMPONENT HEAT FLUXES (LOMBARDO, 1972)

Component	Symbol	Range of Loss or Gain ($kcal/m^2$-day)
Solar radiation	Q_s	1100 → 7600
Reflected solar radiation	Q_r	110 → 550
Net long wave radiation	Q_{an}	6350 → 8150
Net surface radiation	Q_{br}	6500 → 9800
Evaporative heat loss	Q_e	5500 → 20000
Convective heat loss (heat gain)	Q_c	-870 → 1100

For lake simulations, the net external heat flux, H, converted to a single volumetric heat source, is typically assigned to the top layer of fluid with the exception of the net shortwave radiation which is distributed vertically according to Beer's law (see Section 2.3.5). The flow and dispersion regimes then transport this external heat input throughout the entire lake.

The temperature values can either be computed along with the lake circulation in the hydrodynamic model and then be transferred to the water quality model (Tetra Tech, 1975), or a heat budget equation for temperature, analogous to a mass transfer equation formulation, may be used for temperature regime prediction (U.S. Army Corps of Engineers, 1974).

2.3.4 Ice Formation

The formation of a surface ice layer is simulated only in a limited number of lake models (Baca and Arnett, 1976; Tetra Tech, 1976b). The procedure used in modeling ice formation was similar in the two models reviewed.

Baca and Arnett's technique is to monitor the water surface temperature until a temperature of 4°C or less is observed. At this point a continuous accounting is kept of net heat loss (or gain) across the interface. Then when the total heat loss to the atmosphere is equivalent to the heat of fusion for a 5 cm depth of ice, an ice cover is assumed to be formed on the lake's surface. Thereafter, cover thickness is computed by means of the following expression:

$$\Delta = - Q_T/H_F \qquad (2\text{-}50)$$

where Δ = ice thickness, m

Q_T = total heat loss to atmosphere from surface layer, kcal/m^2

H_F = heat of fusion for water (7.97×10^4 kcal/m^3)

Once ice is formed, assumed atmospheric heat exchange is limited to conductance through ice. The heat flux across the air-ice interface is then given by:

$$Q_n = -K\left(T_a - T_s\right)/\Delta \tag{2-51}$$

where Q_n = heat flux transferred across ice by conduction, kcal/m^2-sec

K = conductivity of ice (5×10^{-4} kcal/sec-m-°C)

T_s = temperature of the ice water interface, typically 0°C, but a function of dissolved solids

T_a = air temperature, °C

Over a period of days the total heat flux transferred is equal to the sum of the daily Q_n values where T_a, T_s, and Δ can change on a daily basis.

The approach used by Tetra Tech is very similar. Heat loss is monitored as the water temperature is lowered to 0°C and the overall heat flux is negative. As in Baca and Arnett's formulation, the heat conductance term, H_c, considers heat conductance through the ice layer as the limiting factor:

$$H_c = K_I\left(\frac{T_c - T_d}{D}\right) \tag{2-52}$$

where K_I = thermal conductivity of ice (usually 5×10^{-4} kcal/sec-m-°C)

T_c = temperature of ice at ice-water interface, °C (generally 0°C)

T_d = dry bulb air temperature, °C

D = thickness of ice, m

Once ice is formed, the back radiation from the ice, H_{bI}, can be approximated by:

$$H_{bI} = 0.074 + 0.0012\ T_d \tag{2-53}$$

where H_{bI} = back radiation, kcal/m^2-sec

T_d = dry bulb air temperature, °C

Equation (2-53) is a linear approximation of the Stefan-Boltzman equation (Equation (2-41)).

The problem of estimating ice cover, being related to air temperature, sometimes makes it necessary to forecast long-range air temperatures. Rogers (1976) has analyzed four techniques for making monthly air temperature predictions using wintertime data around Lakes Superior, Huron, and Michigan. Rogers suggested that once an accurate air temperature forecasting technique is devised, it could be applied to ice forecasting since the number of freezing degree-days needed to cause ice formation over many parts of the Great Lakes has been established (Snider, 1974). Accurate ice forecasting in this region can prove beneficial by predicting the number of shipping days available on the Great Lakes and the St. Lawrence Seaway. The four forecasting techniques Rogers examined were:

1. the use of data on climatological cycles and oscillations,

2. the extrapolation and kinematic process used by the National Meteorological Center which provides forecasts in the Average Monthly Weather Outlook,

3. the use of conditional probabilities, and

4. the use of a Markov chain equation (where the outcome of a given trial depends only on the outcome of the immediately preceding trial).

Rogers found that only techniques 1 and 2 improved estimates over that due to chance alone. By combining these two methods, Rogers stated that an improved air temperature forecasting method might be established for application to ice simulation.

2.3.5 Light Attenuation

As discussed previously in Section 2.3.3, only shortwave solar radiation can penetrate the water column. Therefore, the shortwave solar radiation, Q_S, is the only term in the heat budget equation which reaches hydraulic elements below the surface. The amount of light (radiation) reaching a given point within the modeled system is measured in terms of light intensity, which is known to vary as a function of both the time of day and the depth.

The "extinction coefficient," together with the incident shortwave solar radiation, are the variables controlling the light intensity. Empirical fits are usually made to the distribution of these variables in order to describe their effect. Although a single approach is commonly used in river, lake, and estuary modeling studies, coefficients in some instances are system specific.

Baca and Arnett (1976), Lombardo (1972), Di Toro, et al. (1971), Bierman (1976), and Thomann, et al. (1975), all used a modified form of the Beer-Lambert law to describe light attenuation with depth. This law can be described by an equation of the following form:

$$I = I_o e^{-K_e Z} \tag{2-54}$$

where I = light intensity at depth, Z; langleys/min

I_o = intensity of light energy passing the air-water interface after allowances for absorption, scattering, or cloudiness, and reflection at the water surface, langleys/min

Z = depth, m

K_e = extinction coefficient, m^{-1}

Orlob (1974) suggests that values of I_o can be determined by using a pyroheliometer (on a clear day) at the water surface elevation and correcting for cloud interception (when it exists) by multiplying by the factor $(1 - 0.65\ C^2)$ in which C is the cloudiness as a decimal part of the sky covered by clouds. Reflection may also reduce the incident light by an additional 3 to 5%.

Baca and Arnett (1976) modified the extinction coefficient, K_e, to account for algal light absorption as follows:

$$K_e = \alpha_o + \beta \overline{P} \tag{2-55}$$

where α_o = extinction coefficient of water, m^{-1}

β = self-shading factor, per m per mg-C/l

$\overline{P}$ = average phytoplankton concentration above Z, mg-C/l

The light extinction depth (euphotic depth), d, is defined as that depth at which the light intensity is 1% of the incident value. Baca and Arnett (1976) suggest that when the algal attenuation is insignificant, the extinction coefficient, α_o, may be assumed to equal 4.6/d. The extinction coefficient can also be estimated by means of Secchi disk readings where α_o is defined as $1.89/d_s$ and d_s is the Secchi depth, in meters. Values reported for the extinction coefficient range from 0.05 to 0.9 m^{-1} (Baca and Arnett 1976). Baca and Arnett also report values for the self-shading factor, β, ranging from 0.2 to 0.6.

Thomann, et al. (1975), in a modeling study of Lake Ontario, and Lombardo (1972), suggested the following expression for the extinction coefficient:

$$K_e = \alpha_o + 0.0088P + 0.054\, P^{0.66} \qquad (2\text{-}56)$$

where α_o = light extinction coefficient at zero chlorophyll concentration

P = phytoplankton chlorophyll, μg/l

Bierman (1976), also distributing light with depth according to the Beer-Lambert law, proposed the following formulation for the extinction coefficient:

$$K_e = 1.9/d_s + 0.17 \cdot \text{TCROP} \qquad (2\text{-}57)$$

where d_s = Secchi depth, m

TCROP = total phytoplankton biomass, mg dry weight/l

Lombardo (1972) also reports a range of values for the self-shading factor, β, given by Talling as: 0.00304 to 0.00608 $(\text{ft-}\mu\text{g Chl/l})^{-1}$.

Tetra Tech (1976b) uses a term similar to that suggested by Baca and Arnett (1976) for determining the extinction coefficient, K_e:

$$K_e = \alpha_o + \Sigma r_i\, S_i \qquad (2\text{-}58)$$

where α_o = light extinction coefficient of water with no suspended matter, m^{-1}

r_i = self-shading coefficient of constituent i

S_i = concentration of suspended matter, i, mg/l (detritus, sediment, algae)

In describing the variability of light intensity with time, Di Toro, et al. (1971) express the incident solar radiation, I_o, as a function of the time of day according to the following criteria:

$$I_o(\text{day}) = I_a \tag{2-59}$$

$$I_o(\text{night}) = 0 \tag{2-60}$$

where I_a = average incident solar radiation intensity during photoperiod

Baca and Arnett (1976) used the following equation of "standard light day" proposed by Vollenweider to account for the diurnal pattern of incident light:

$$\begin{gathered} I_o(t) = 1/2\ I_{max}\left(1 + \cos\left(\frac{2\pi t}{\lambda}\right)\right),\ -\lambda/2 \leq t \leq \lambda/2 \\ I_o(t) = 0, \text{ for remaining } 24-\lambda \text{ hrs of day} \end{gathered} \tag{2-61}$$

where t = time, hrs

λ = day length factor, hrs

I_{max} = maximum instantaneous light intensity

I_{max} is calculated from the total daily solar radiation such that the integral of I_o over one day equals the total daily radiation. The day length factor, λ, is given as a function of time and latitude as follows*:

$$\lambda = \frac{24}{\dfrac{\pi}{\cos^{-1}\left(-\tan(\gamma_o)\tan(\delta)\right)}} \tag{2-62}$$

where γ_o = latitude, radians

δ = declination, radians = $0.409 \sin(0.0172\ N_d - 1.3762)$ and N_d equals the Julian day number

In their formulation for describing the variation of light intensity with time, Tetra Tech (1975) uses the following expression in order to obtain a "constant average daily light intensity":

---

*Equation (2-62) as given by Baca and Arnett (1976) was in error. Version is correct as shown here.

$$LI = \frac{TSR}{.75\ DH} \qquad (2\text{-}63)$$

where LI = constant average daily light intensity

TSR = total shortwave radiation

DH = duration of daylight hours

2.4 BIOLOGICAL PROCESSES

2.4.1 Fish

The behavior of fish, as a function of food supply, concentration of oxygen and toxic substances, and temperature, is known only in general terms. Where fish are included in models it is primarily to indicate population trends rather than to predict precise biomass levels. Fish are generally modeled in a manner similar to that used for phytoplankton and zooplankton, and are assumed to graze primarily on zooplankton and/or benthic animals.

Since they are actively motile, fish are generally not assumed to be advected or diffused, but to migrate to locations favorable for feeding or reproduction and away from locations that are unfavorable for their life processes. This is usually simulated in the models by distributing fish to elements in proportion to the densities of the food within the element.

Fish are usually grouped in one of two ways in modeling studies. They can be distinguished according to their feeding habits and temperature preference, as well as by various life stages. In its Lake Ontario model, Tetra Tech (1975), established fish groups according to both criteria. The following four groups of fish were chosen: 1) cold water, 2) warm water, 3) forage, and 4) scavenger. For each group, three life stages were assumed: 1) eggs and larvae, 2) young, and 3) adult. The eggs and larvae group is assumed to behave like zooplankton--grazing on algae and detritus. Members of the group are consumed by all young fishes and adult alewife. Young fish graze on zooplankton and fish larvae, and are in turn preyed upon by adult fishes.

In another modeling study, Tetra Tech (1976b) considered only three groups of fish: 1) cold water, 2) warm water, and 3) scavenger. Similarly, the U.S. Army Corps of Engineers (1974) and Chen and Orlob (1975) suggest dividing the fish population into three separate groups.

Generally, a mass balance formulation describing the rate of change of each fish group's biomass is included in the water quality model. Kelly (1975) uses the following typical representation to describe changes in fish biomass:

$$\frac{d(Fish)}{dt} = \text{FEEDING} - \text{RESPIRATION} - \text{DEATH} - \text{EXCRETION} \qquad (2\text{-}64)$$

where each term on the right-hand side may be further described by an empirical expression.

Tetra Tech (1975) suggests the following similar type of formulation:

$$S = FISH \cdot (FG - FM - FR) + GRADIN - GRADOT - FGRAZ - HARVST \qquad (2\text{-}65)$$

where FISH = fish biomass at a given life stage, mg/l or g/m^2

FG = growth rate, day^{-1}

FM = mortality rate, day^{-1}

FR = respiration rate, day^{-1}

GRADIN = spawning or recruitment rate, mg/l-day

GRADOT = maturation rate to next life stage, mg/l-day

FGRAZ = grazing rate, mg/l-day

HARVST = harvest rate, mg/l-day

S = change in fish biomass day^{-1}

The fish growth rate, FG (mg/l-day), may be defined as follows (U.S. Army Corps of Engineers, 1974):

$$FG = FMAX \cdot \left(\frac{ZB}{ZB_2 + ZB} \right) \qquad (2\text{-}66)$$

where FMAX = maximum specific growth rate of fish at 20°C, day^{-1}

ZB = quantity of zooplankton or benthic animals available for grazing, mg/l

ZB_2 = half-saturation constant for fish grazing on zooplankton or benthic animals, mg/l

The fish growth rate in some approaches is also assumed to be a function of temperature and food density. For each fish group, a satisfactory temperature range is provided. Fish growth computations are not performed when the simulated temperature is outside their growth range, or when DO is too low to sustain a healthy fish population.

Tetra Tech (1975), in their Lake Ontario model, suggested that preference factors be specified in accordance with the known food preference of each group of fish. The effective food density would then be calculated as follows:

$$\text{FOOD} = \Sigma \left(\text{PREY} \cdot \text{PREF}\right) \qquad (2\text{-}67)$$

where FOOD = effective food density, mg/l

PREF = preference factor, unitless

PREY = density of prey, mg/l

Table 2-8 presents a listing of coefficient values commonly used in mass balance formulations for various fish groups.

Recently, Leidy and Jenkins (1977) have prepared an extensive document on fish in ecosystem modeling. Tables 2-9 through 2-12 have been reproduced from that report.

2.4.2 Detritus

Detritus is the term used to describe organic material suspended in the water column. Sources of detritus may be phytoplankton and zooplankton mortality, fish excretions, and tributary contributions. Losses or sinks of detritus are generally through sedimentation and decay. The bacterial and physical breakdown of detritus involves a large number of complex reactions, most of which have been inadequately investigated (Canale, et al., 1976).

The amount of detritus present at any time is usually simulated by means of a mass balance expression (Tetra Tech, 1975; Tetra Tech, 1976b; U.S. Army Corps of Engineers, 1974; Chen and Orlob, 1975; Chen and Wells, 1975). Detritus decay is generally formulated by means of a linear first order differential equation. A typical mass balance expression, similar to those used by Tetra Tech (1975, 1976b) and the U.S. Army Corps of Engineers (1974), is given as:

$$\begin{aligned} d\text{DET}/dt = &-\text{DET}\ (\text{DQTEN} + \text{DSETL}) + \text{FISH} \cdot \text{FM} + \text{ZFEX} \\ &\cdot \text{FDET} + \text{ZOO} \cdot \text{ZM} + \text{ZEX} \cdot \text{ZDET} \end{aligned} \qquad (2\text{-}68)$$

where DET = detritus concentration, mg/l

DQTEN = temperature adjusted decay rate, day^{-1}

DSETL = detritus settling velocity, day^{-1}

FISH = fish larvae, mg/l

FM = larvae mortality rate, day^{-1}

ZFEX = high excretion rate (young and adult) mg/l-day

TABLE 2-8. VALUES FOR COEFFICIENTS USED IN FISH MASS BALANCE FORMULATIONS

Fish Group	System Modeled	Maximum Specific Growth Rate @ 20°C, days^{-1}	Half-Saturation Constants for Grazing			Respiration Rate, day^{-1}		Reference
			Fish on Zoo. mg/l	Fish on Benthos mg/m^2	Fish on Insects mg/m^2	Active	Inactive	
Cold Water	N. Fork, Kings River, CA	0.025	0.20	--	--	0.002	0.0002	Tetra Tech (1976b)
Warm Water	"	0.03	0.20	--	--	0.002	0.0002	Tetra Tech (1976b)
Scavenger	"	0.025	--	500	--	0.002	0.0002	Tetra Tech (1976b)
Cold Water	Trinity R., Texas	0.02-0.03	0.05-0.01	--	--	0.001-0.01	0.0001-0.005	U.S. Army Corps of Engineers (1974)
Warm Water	"	0.02-0.03	0.05-0.01	--	--	"	"	U.S. Army Corps of Engineers (1974)
Scavenger	"	0.02-0.03	--	50-2000	--	"	"	U.S. Army Corps of Engineers (1974)
Cold Water	Lake Washington	0.02	0.05	--	--	0.001	--	Chen and Orlob (1975)
Warm Water	"	0.03	0.01	--	--	0.001	--	Chen and Orlob (1975)
Scavenger	"	0.02	--	500	--	0.001	--	Chen and Orlob (1975)
Plankton Feeder	S.F. Bay Estuary	0.03	0.05	--	--	0.001	--	Chen (1970)
Scavenger	"	0.02	--	500	--	0.001	--	Chen (1970)
Cold Water	Boise R. Idaho	0.03	0.05	--	--	0.001	--	Chen and Wells (1975)
Warm Water	"	0.03	0.05	--	--	0.001	--	Chen and Wells (1975)
Scavenger	"	0.025	--	500	500	0.001	--	Chen and Wells (1975)

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(continued)

TABLE 2-8 (continued)

Fish Group	System Modeled	Mortality Rate day-1	Chemical Composition C	Chemical Composition N	Chemical Composition P	Temperature Tolerance Range, °C	Reference
Cold Water	N. Fork, Kings River, CA	0.002	0.4	0.08	0.015	5-20	Tetra Tech (1976b)
Warm Water	"	0.002	0.4	0.08	0.015	10-30	Tetra Tech (1976b)
Scavenger	"	0.002	0.4	0.08	0.015	5-30	Tetra Tech (1976b)
Cold Water	Trinity R., Texas	0.001- 0.005	0.4- 0.5	0.07- 0.09	0.01- 0.012	--	U.S. Army Corps of Engineers (1974)
Warm Water	"	"	"	"	"	--	U.S. Army Corps of Engineers (1974)
Scavenger	"	"	"	"	"	--	U.S. Army Corps of Engineers (1974)
Cold Water	Lake Washington	--	--	--	--	--	Chen and Orlob (1975)
Warm Water	"	--	--	--	--	--	Chen and Orlob (1975)
Scavenger	"	--	--	--	--	--	Chen and Orlob (1975)
Plankton Feeder	S.F. Bay Estuary	--	--	--	--	--	Chen (1970)
Scavenger	"	--	--	--	--	--	Chen (1970)
Cold Water	Boise R. Idaho	--	0.5	0.09	0.015	--	Chen and Wells (1975)
Warm Water	"	--	0.5	0.09	0.015	--	Chen and Wells (1975)
Scavenger	"	--	0.5	0.09	0.015	--	Chen and Wells (1975)

TABLE 2-9. TEMPERATURE TOLERANCES FOR VARIOUS FISH GROUPS*
(AFTER LEIDY AND JENKINS, 1977)

Species Group	Lower Lethal	Optimum for Growth	Upper Lethal
Pickerel	0	25.4	34.4
Minnows	0	27	33.4
Catfish	0	30	37.1
Sunfish	≤ 2.5	27.5	35.7
Black bass	≤ 1.6	27	36.5
Crappies		≈23	32.5
Yellow perch	0	24.2	30.9
Average values	0	26.3	34.8

*All values expressed in degrees C.

TABLE 2-10. CHEMICAL COMPOSITION OF FISH (AFTER LEIDY AND JENKINS, 1977)

Element and Species	% Composition		Reference
	Dry Weight	Wet Weight	
Nitrogen (N)			
Ocean sunfish (Mola mola)	16.6-18.2		Green (1899)
Bluegill	16.7		Calculated from data by Geng (1925), Gerking (1962), and Maynard (1951)
Bluegill		2.72	Gerking (1962)
Carp		2.6	Bull and MacKay (1976)
Northern squawfish		2.5 ± 0.1	
Largescale sucker		2.4	
Rainbow trout		2.9	
Channel catfish		2.35	Worsham (1975)
General average	16.3		Bailey (1937), Nottingham (1952)
Carbon (C)			
Ocean sunfish (Mola mola)	48.2		Green (1899)
Phosphorus (P)			
Salmon		0.59	Atwater (1892) as P_2O_5
Trout		0.81	
Cod		0.60	
Eel		0.68	
Haddock		0.97	
Halibut		0.44	
Herring		0.56	
Mackerel		0.56	
Turbot		0.48	
Average of above species		0.63	
Bluegill	4.75 ± 0.70 4.73 ± 0.85		Kitchell, et al. (1975) ± 1 S.E.
Bluegill	4.2		Hall, et al. (1970)
Channel catfish		0.86	Worsham (1975)
Carp		0.5 ± 0.01	Bull and MacKay (1976)
Northern squawfish		0.4	
Largescale sucker		0.3	
Rainbow trout		0.4	
General average (for fish flesh)		0.22 (range: 0.1-0.4)	Clauseret (1962)

TABLE 2-11. ESTIMATED HALF-SATURATION CONSTANTS FOR FISH GROWTH (AFTER LEIDY AND JENKINS, 1977)

Species	Length and/ or Weight	Water Temperature °C	Calculated Maximum Growth Rate Expressed as % of Body Weight Gained Per Day	Calculated Half-Saturation Constant (K_S) Expressed as % of Body Weight Consumed Per Day	Type of Food	Reference
Largemouth bass	24.5 cm	21	3.9	4.6	minnows	Thompson (1941)
Smallmouth bass	8.3-20.2 cm 4-112 g (mean wt.=40 g)	21.3	4.7	7.2	minnows	Williams (1959)
Muskellunge	17.0 cm 17.0 g	19.5	3.9	5.6	minnows	Gammon (1963)
Reticulate sculpin	1.2 g	11.6	1.7	4.4	midge larvae	Davis and Warren (1965)
Channel catfish	4 g	30	3.4	3.1	mixed diet	Andrews and Stickney (1972)
Sockeye salmon	6.9 g	10	1.8	3.9	mixed diet	Brett, *et al.* (1969)
Sockeye salmon	7.1 g	15	4.2	7.9	mixed diet	Brett, *et al.* (1969)

TABLE 2-12. FISH FOOD EXPRESSED AS A PERCENTAGE OF THE DIET BY VOLUME*
(AFTER LEIDY AND JENKINS, 1977)

Species or Species Group	FOOD					
	Plant	Detritus	Benthos	Zooplankton	Fish	Terrestrial
Gars					100	
Bowfin					100	
Gizzard shad	10	80	5	5		
Threadfin shad (young)	30	50	10	10		
Threadfin shad (adult)	30	5	15	55		
Rainbow trout	5		60	15	10	10
Brook trout			90	5		5
Pickerels					100	
Carp	30	40	20	10		
Minnows	20		20	60		
Carpsuckers	15	65	5	15		
Suckers	15	65	5	15		
Hog suckers		80	5	15		
Buffalofishes	5	40	5	50		
Redhorses			100			
Bullheads	10	25	50		15	
Catfishes	10		10		80	
Madtoms		27	55		18	
Silversides			20	80		
Temperate basses			20	10	70	
Sunfishes	10	5	65		5	15
Black basses			8		86	6
Crappies	5	5	20	15	55	
Perches			20	20	60	
Freshwater drum		8	58		34	
All other species			100			

*Food categories are described in the text of the original reference.

FDET = detritus fraction of fish excreta, unitless

ZOO = zooplankton concentration, mg/l

ZM = zooplankton mortality, day^{-1}

ZEX = zooplankton excretion rate, mg/l-day

ZDET = detritus fraction of zooplankton excreta, unitless

The detritus decay rate term, DQTEN, is temperature adjusted with a typical correction expression as follows:

$$\text{DQTEN} = \text{DQTEN}_{(20°\text{C})}\ \theta^{(T-20)} \qquad (2\text{-}69)$$

where θ = temperature coefficient

T = temperature, °C

Table 2-13 is a list of coefficient values commonly used in mass balance formulations for detritus. The decay of detritus is typically associated with a resulting oxygen demand. The usual procedure in accounting for this demand is to include a term for detritus in the dissolved oxygen mass balance expression. With this term, the amount of detritus decayed is converted to oxygen utilized by means of a stochiometric coefficient. Various values used for this coefficient are also listed in Table 2-13.

2.4.3 Benthic Organisms

Tetra Tech (1975, 1976b), Chen and Orlob (1975), Chen and Wells (1975), and the U.S. Army Corps of Engineers (1974) are some of the relatively few investigators who include mass balance formulations for benthic animals in their water quality models. The benthic animal expressions are formulated in the same manner as for zooplankton except that settled detritus (organic sediment) is the main food source rather than algae. Benthic animals are assumed to be preyed upon by scavenger fish species. A typical mass balance expression is as follows:

$$\partial B/\partial t = B \cdot KB \cdot (BG-BM-BR) - BGZ \qquad (2\text{-}70)$$

where B = equivalent concentration of benthic animals = BEN · AV, g/m^3

BEN = benthic animal biomass per unit area, g/m^2

AV = ratio of average cross-sectional area to volume of fluid element, m^{-1}

KB = biota activity rate coefficient at local temperature, day^{-1}

TABLE 2-13. VALUES FOR COEFFICIENTS USED IN DETRITUS FORMULATIONS

Detritus Decay Rate @ 20°C (day^{-1})	Temperature Coefficient, θ	Settling Velocity m/day	Stoichiometric Equivalence (O_2/Detritus)	Chemical Composition			Location of Study	Reference
				C	N	P		
0.005	1.03	0.25	1.2	0.4	0.08	0.015	N. Fork Kings River, California	Tetra Tech (1976b)
0.001-0.02	-	0.-2.	-	-	-	-	-	U.S. Army Corps of Engineers (1974)
0.001	-	0.2	2.0	-	-	-	Lake Washington	Chen and Orlob (1975)
0.001	1.02	0.5 ft/day	2.0	-	-	-	San Francisco Bay Estuary	Chen (1970)
0.01	-	0.5 ft/day	2.0	0.2	0.05	0.007	Boise River, Idaho	Chen and Wells (1975)

BG = benthic animal growth rate @ 20°C, day^{-1} = BMAX · (SED/SED$_2$ + SED)

BMAX = maximum specific growth rate @ 20°C, day^{-1}

SED = quantity of organic sediment per unit area, mg/m^2

SED$_2$ = half-saturation constant for benthic animals grazing on organic sediment, mg/m^2

BM = benthic animal mortality rate @ 20°C, day^{-1}

BR = benthic animal respiration rate @ 20°C, day^{-1}

BGZ = quantity of benthic animals grazed by fish = F$_2$B · FBEN/FEFF

F$_2$B = benthic animal portion of the bottom feeding fish diet, unitless fraction

FBEN = fish growth attributed to grazing in benthic animals, g/m^3-day

FEFF = digestive efficiency of fish, unitless fraction

Table 2-14 presents a listing of the values used for the various coefficients in the above formulation for benthic organisms.

2.4.4 Sediment Deposits

Sediment deposits are composed of organic and inorganic material which has settled to a river, lake, or estuary bottom. The source of this organic material may be sewage effluents, settling of organic matter from run-off and inflow streams, and/or photosynthetic production. Settling of algae and detritus, and mortality of fish and benthic animals can also contribute to organic sediment concentrations.

Nutrients in the sediment, both the organic and inorganic fractions, can significantly influence the nutrient content of the water column. The direction of nutrient flux often oscillates with time, and nutrients in the system may be either deposited in, or released from, the bottom environment depending on the controlling conditions.

Fillos and Molof, as reported by Lombardo (1972), obtained data on releases from sediment deposits, as given in Table 2-15 below.

TABLE 2-14. VALUES FOR COEFFICIENTS USED IN BENTHIC ORGANISM FORMULATIONS

Benthic Animal Maximum Growth Rate, @20°C (days^{-1})	Benthic Animal Respiration Rate @ 20°C (days^{-1})	Michaelis Constants	Benthic Animal Mortality Rate @20°C (days^{-1})	Chemical Composition			Location of Study	Reference
		Benthos on Sediment, mg/m^2		C	N	P		
0.03	0.002 (active) 0.001 (inactive)	1,000	0.003	0.4	0.08	0.015	N. Fork Kings River, California	Tetra Tech (1976b)
0.02-0.03	0.001-0.01 (active) 0.0001-0.001 (inactive)	50-2,000	0.001	-	-	-	-	U.S. Army Corps of Engineers (1974)
0.03	0.001	100	-	-	-	-	Lake Washington	Chen and Orlob (1975)
0.05	0.001	100	-	-	-	-	San Francisco Bay Estuary	Chen (1970)
0.05	0.01	50	-	0.5	0.09	0.015	Boise River, Idaho	Chen and Wells (1975)

TABLE 2-15. RELEASE RATES FROM SEDIMENT DEPOSITS (LOMBARDO, 1972)

Constituent	Aerobic Rate	Anaerobic Rate
BOD	0.061 g/m^2-hr	0.203 g/m^2-hr
COD	0.154 g/m^2-hr	0.495 g/m^2-hr
PO_4-P	0.125 mg/m^2-hr	0.250 mg/m^2-hr
NH_3-N	0.1083 mg/m^2-hr	0.3125 mg/m^2-hr

Tetra Tech (1975, 1976b), Chen and Wells (1975), and the U.S. Army Corps of Engineers (1974) formulate a separate mass balance expression for organic sediment, assuming organic sediment decays by first order kinetics and releases nitrogen, phosphorus, and CO_2 according to its stoichiometric composition. A typical formulation is as follows:

$$\begin{aligned} d\left(\mathrm{CSED}\right)/dt = & -\underbrace{\mathrm{SQTEN} \cdot \mathrm{CSED} \cdot \left(1-\mathrm{SSINK}\right)}_{\text{Decay}} - \underbrace{\frac{\mathrm{SGRAZ}}{\mathrm{PEFF}}}_{\substack{\text{Benthic}\\ \text{Grazers}}} \\ & + \underbrace{\mathrm{DET} \cdot \mathrm{DSETL} \cdot \mathrm{BOTTOM}}_{\text{Detritus}} + \underbrace{\mathrm{CBEN} \cdot \mathrm{BM}}_{\substack{\text{Benthic}\\ \text{Death}}} \\ & + \underbrace{\mathrm{BEX} \cdot \mathrm{BDET}}_{\substack{\text{Benthic}\\ \text{Excretion}}} + \underbrace{\mathrm{FISH} \cdot \mathrm{FM} \cdot \mathrm{BOTTOM}}_{\text{Fish Death}} + \underbrace{\mathrm{ALG} \cdot \mathrm{PSETL} \cdot \mathrm{BOTTOM}}_{\text{Algal Death}} \end{aligned} \tag{2-71}$$

where SQTEN = temperature adjusted decay rate, day^{-1}

CSED = organic sediment concentration, mg/m^2

SSINK = refractory fraction of organic sediment, unitless

SGRAZ = grazing rate by benthic animals and fish, mg/m^2-day

PEFF = digestive efficiency of grazer, unitless

DET = detritus concentration, mg/l

DSETL = detritus settling rate, day^{-1}

BOTTOM = conversion factor from mg/l to mg/m^2

CBEN = benthic animal density, mg/m^2

BM = benthic animal mortality rate, day^{-1}

BEX = benthic animal excretion rate, day^{-1}

BDET = organic particulate fraction of excreta, unitless

FM = larval mortality, day^{-1}

FISH = fish larvae, mg/l

ALG = algal density, mg/l

PSETL = settling, day^{-1}

The value used by Tetra Tech (1976b) for the sediment decay rate coefficient in their modeling study of the North Fork Kings River, California was 0.001 day^{-1} at 20°C. The U.S. Army Corps of Engineers (1974) reported a range of values for the sediment decay rate from 0.001 to 0.02 day^{-1}. Chen and Wells (1975) report that the lower rate (0.001 day^{-1}) is applicable to organic matter associated with algal cell decomposition. In their Boise River, Idaho modeling study, the organic deposits resulted primarily from sewage inflows and were readily oxidizable. Therefore, a decay rate value of 0.01 day^{-1} was chosen.

Several other model formulations for sediment deposits (Baca and Arnett, 1976; and Lerman, 1971) are primarily concerned with the nutrient changes which occur within the sediments. Mass balance expressions specifically for organic sediment are generally not used by these investigators. Rather, the usual procedure is to include terms for sediment release and deposition within the complete mass balance expression for the specified nutrients (constituents) of concern. The formulations for the sediment term or terms vary from model to model, and from study to study.

Baca and Arnett's (1976) model considers the loss of both organic and inorganic phosphorus to the sediments, and anaerobic releases of certain nutrients from the sediments. The sediment nutrient terms are included in a mass balance expression for sediment phosphorus as follows:

$$\frac{dD_3}{dt} = I_1 D_1 + I_4 D_2 - I_3 D_3 \qquad (2\text{-}72)$$

where D_3 = sediment phosphorus, mg/l

D_2 = water column organic phosphorus, mg/l

D_1 = inorganic phosphorus, mg/l

I_1 = rate constant for loss to sediment, day^{-1}; typically 0.1-0.7

I_3 = rate constant for sediment release, day^{-1}; typically 0.1-0.7

I_4 = rate for organic phosphorus loss to sediments, day^{-1}; typically 0.01-0.1

A similar type of formulation was used by Baca and Arnett (1976) for sediment nitrogen.

Lam and Jacquet (1976) have developed a model which includes a detailed simulation of the physical transport and regeneration of phosphorus in Lake Erie. In their model, sediment resuspension is considered to occur as a result of movement of the water at the bottom caused by surface waves only. Resuspension from nonperiodic currents was not considered for the following reasons:

1. The general current pattern and velocities are computed from water transport and velocities are depth averaged. This assumption makes computation of actual bottom current velocities difficult.

2. For practically all time periods considered in applications to Lake Erie, the bottom orbital velocities were about one order of magnitude higher than computed current velocities.

The following steps were followed by Lam and Jacquet in order to represent the physical regeneration process: 1) starting with wind speed and direction, relevant wave parameters were obtained from a wave hindcasting method and used to compute bottom orbital velocities; 2) sediment resuspension was then expressed as a function of this velocity; and finally 3) phosphorus regeneration was estimated by taking into account its distribution in sediments.

Lerman (1971) reports that his model, designed for simulation of lakes or impoundments, may be applied to situations where chemical species are formed at the sediment-water interface. The model is capable of simulating the transport of these released materials upwards by eddy diffusion. Lombardo's (1972) model simulates scour in rivers by doubling the release rates when the river velocity is greater than 10 fps.

2.5 CHEMICAL PROCESSES

2.5.1 Nitrogen Cycle

The major constituents comprising the nitrogen cycle are detrital organic nitrogen (org-N), ammonia nitrogen (NH_3-N), and nitrate nitrogen (NO_3-N), with gaseous nitrogen being important when organisms are present having nitrogen fixation capabilities. In natural aerobic waters there is a stepwise transformation from organic nitrogen to ammonia, to nitrite, and to nitrate, a process which yields nutrients for phytoplankton growth. The chain of reactions comprising the nitrogen cycle are illustrated in Figure 2-13, as given by Canale, et al. (1976). Also depicted in this figure are some of the mechanisms of nutrient recycling.

Different authors, depending on their particular concern, will emphasize various aspects of the nitrogen cycle, or emphasize a specific nitrogen cycle applicable to the system they are studying. As examples, Kormondy (1969) discusses a more general nitrogen cycle, from a biological and ecological viewpoint, than that shown in Figure 2-13. Brezonik (1973) emphasizes the nitrogen cycle reactions occurring in an idealized lake environment, while Harleman, et al. (1977) illustrate a nitrogen cycle applicable to aerobic estuaries, and apply it in water quality model development.

Kinetics of the transformations of nitrogen forms are generally assumed to be first order reactions with temperature-dependent rate coefficients. Source/sink formulations are developed to describe the rates of change of the major nitrogen forms. These formulations are incorporated into complete mass balance expressions which also consider the physical transport of the various nitrogen constituents throughout the system by means of advection and diffusion.

Sources of organic nitrogen, which contribute to the nitrogen concentration in aquatic systems, are generally considered to be due to the following processes: 1) respiration of algae and zooplankton, 2) natural death of zooplankton, and 3) external sources of organic nitrogen such as wastewater discharges. In a few extensive nutrient submodels, a source of organic nitrogen due to the grazed but unassimilated portion of phytoplankton which is excreted by zooplankton is considered (see, for example, Thomann, et al. (1975)).

A typical formulation for the organic nitrogen source/sink term is given as (Lorenzen, et al., 1974):

$$dC_4/dt = -J_4 C_4 + D_p P A_{np} + D_z Z A_{nz} \qquad (2\text{-}73)$$

where D_p = specific algal death rate, day^{-1}

D_z = specific zooplankton death rate, day^{-1}

P = phytoplankton concentration, mg-C/l

Z = zooplankton concentration, mg-C/

A_{nz} = N to C ratio for zooplankton, mg-N/mg-C

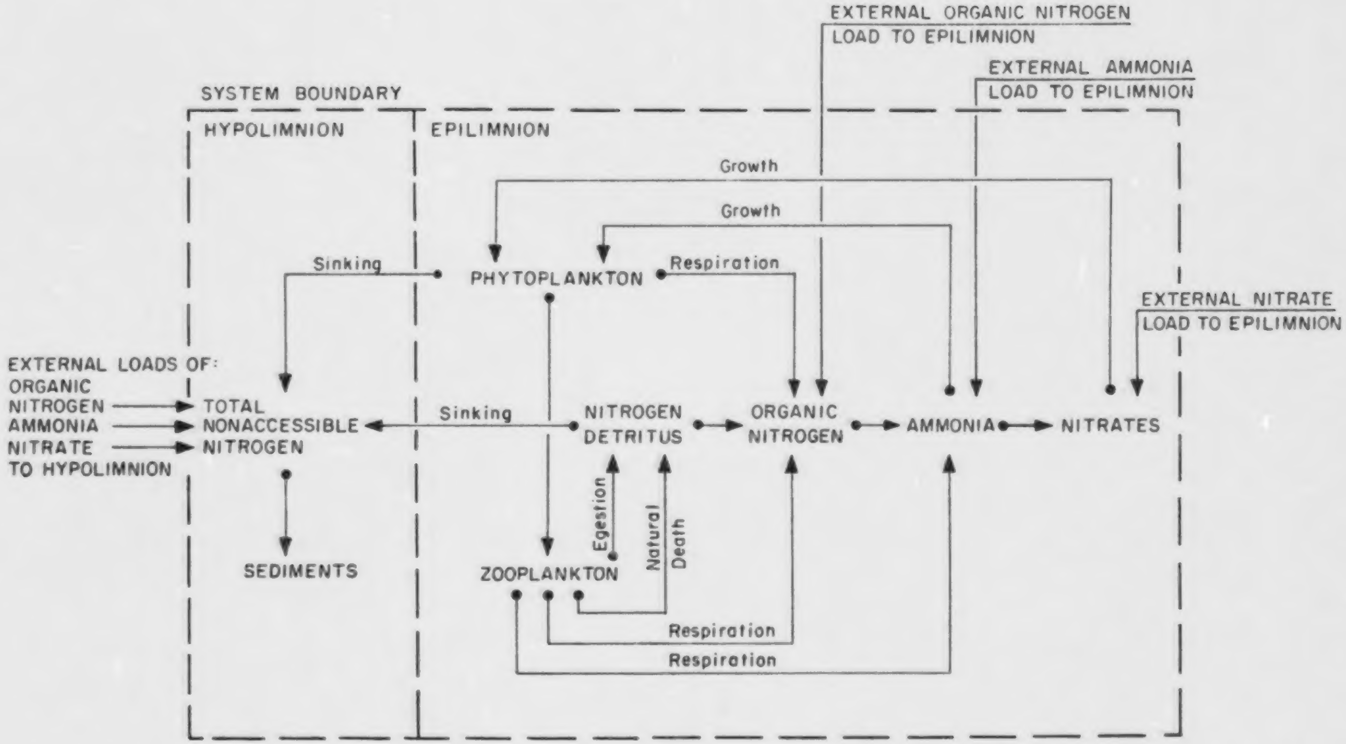
EXTERNAL ORGANIC NITROGEN
LOAD TO EPILIMNION
EXTERNAL AMMONIA
LOAD TO EPILIMNION
SYSTEM BOUNDARY
HYPOLIMNION
EPILIMNION
Growth
Growth
Sinking
PHYTOPLANKTON
Respiration
EXTERNAL NITRATE
LOAD TO EPILIMNION
EXTERNAL LOADS OF:
ORGANIC
NITROGEN
AMMONIA
NITRATE
TO HYPOLIMNION
TOTAL
NONACCESSIBLE
NITROGEN
Sinking
NITROGEN
DETRITUS
ORGANIC
NITROGEN
AMMONIA
NITRATES
Egestion
Natural
Death
SEDIMENTS
ZOOPLANKTON
Respiration
Respiration

Figure 2-13. Pathways used in modeling the nitrogen cycle (modified after Canale, et al., 1976).

A_{np} = N to C ratio for phytoplankton, mg-N/mg-C

J_4 = rate constant for organic nitrogen decay, day^{-1}

C_4 = organic nitrogen concentration, mg/l

In this simplified expression, the endogenous respiration of phytoplankton is represented in the specific death rate term for phytoplankton. Similarly, the endogenous respiration of zooplankton is incorporated into the zooplankton specific death term. Settling effects and the unassimilated portion of grazed algae are not included in the formulation.

Various investigators have used similar expressions to suit the needs of their particular model application. Baca and Arnett (1976) use the following formulation, which neglects organic nitrogen sources due to zooplankton excretion but additionally considers zooplankton grazing and settling of organic nitrogen.

$$dC_4/dt = -J_4 C_4 + D_p - C_g Z P A_{np} + D_z Z A_{nz} - J_6 C_4 \qquad (2\text{-}74)$$

where C_g = zooplankton grazing rate, day^{-1}

A_{nz} = nitrogen to carbon ratio for zooplankton, mg-N/mg-C; typically 0.05-0.17

J_6 = sediment uptake rate, day^{-1}; typically 0.0-0.01

Both Anderson, et al. (1976) and Lombardo (1972) have included source/sink formulations for organic nitrogen in their nitrogen submodels, which consider processes similar to those simulated by Baca and Arnett (1976). Both submodels consider organic nitrogen concentration changes to be due to: 1) zooplankton excrement, death, respiration, and decay; and 2) phytoplankton respiration and decay.

Canale, et al. (1976), in their nitrogen cycle submodel, consider nitrogen detritus and organic nitrogen as separate constituents (Figure 2-13). The nitrogen detritus is considered to be removed from the system by both settling and decay to dissolved organic nitrogen. Canale noted that the reaction rate for the breakdown of detrital forms into dissolved organic forms was not readily available in the literature. For the Lake Michigan application, this rate was set equal to the rate used for the conversion of organic nitrogen to ammonia. Canale's inclusion of two different formulations for the organic nitrogen concentration effectively separates the entire set of reactions into two distinct groups, and allows application of different rate coefficients to each group of reactions.

Canale, et al. (1976) used the following equation to describe changes in detrital nitrogen:

$$dDN/dt = NCR \cdot \sum_z \left(\left(1 - \begin{bmatrix} \text{assimilation} \\ \text{efficiency} \end{bmatrix}_z \right) \cdot \begin{bmatrix} \text{eating} \\ \text{rate} \end{bmatrix}_z \cdot C_z \right)$$

$$+ NCR \cdot \begin{bmatrix} \text{natural} \\ \text{death} \end{bmatrix} - A18 \cdot T \cdot DN - A23 \cdot SINK\ (t) \cdot DN \qquad (2\text{-}75)$$

where NCR = nitrogen to carbon ratio by weight, unitless

z = zooplankton species subscript

C_z = zooplankton concentration for species z, mg/l

A18 = detrital nitrogen to dissolved organic nitrogen decay rate, day^{-1}

A23 = detrital sinking rate, day^{-1}

DN = detrital nitrogen concentration, mg/l

T = water temperature, °C

SINK = seasonal variation adjustment factor, unitless

The first term in the expression represents the contribution due to zooplankton excretion and the second term refers to the natural death of the various zooplankton species. The third and fourth terms represent a first order decay to organic nitrogen and settling losses, respectively.

The expression for dissolved organic nitrogen is given by Canale et al. (1976) as:

$$dORGN/dt = NCR \cdot \sum_p \begin{bmatrix} \text{respiration} \\ \text{loss} \end{bmatrix}_p + NCR \cdot A21 \cdot \sum_z \begin{bmatrix} \text{respiration} \\ \text{loss} \end{bmatrix}_z$$

$$+ A18 \cdot T \cdot DN - A20 \cdot T \cdot ORGN + LOAD_{15} \qquad (2\text{-}76)$$

where ORGN = dissolved organic nitrogen concentration, mg/l

p = phytoplankton species subscript

A21 = fraction of zooplankton respired nitrogen that is organic, unitless; typically 0.7

A20 = organic nitrogen to ammonia nitrogen decay rate, $(\text{day} - {}^{\circ}\text{C})^{-1}$

LOAD_{15} = loading rate of dissolved organic nitrogen, mg/epilimnion 1-day

Dissolved organic nitrogen forms are generated during phytoplankton respiration. Approximately 70% of the nitrogen respired by zooplankton is assumed to enter the water in an organic form, with the remaining as ammonia nitrogen.

Thomann, et al. (1975) considered two sources of detrital organic nitrogen in their submodel: 1) organic nitrogen produced by the endogenous respiration of phytoplankton and zooplankton (assuming only organic forms of nitrogen result from this process), and 2) the organic nitrogen equivalent of grazed, but nonmetabolized phytoplankton excreted by zooplankton. They use a single expression of the following form to describe the total organic nitrogen balance:

$$dORGN/dt = a_1\, D_p\, P + \frac{a_1}{a_c} D_z\, Z + \frac{a_1}{a_c} P \left[1 - \frac{a_{zp} K_{mp}}{K_{mp} + P} \right] C_g Z - K_o\, C_4 - K_s\, C_4 \qquad (2\text{-}77)$$

where a_1 = nitrogen to chlorophyll ratio, unitless

D_p = specific phytoplankton death rate, day^{-1}

P = phytoplankton concentration as chlorophyll, mg/l

a_{zp} = zooplankton carbon to phytoplankton chlorophyll efficiency, unitless

a_c = carbon to chlorophyll ratio, unitless

D_z = specific zooplankton death rate, day^{-1}

Z = zooplankton concentration as carbon, mg/l

K_{mp} = Michaelis constant for zooplankton grazing on phytoplankton, mg/l

C_g = zooplankton grazing rate, $\text{day}^{-1}\ (\text{mg/l})^{-1}$

K_o = decay rate of organic nitrogen to ammonia, 1/day

K_s = removal rate due to settling or additional decay, day^{-1}

C_4 = organic nitrogen concentration, mg/l

The first and second terms represent organic nitrogen released through endogenous respiration by the phytoplankton and zooplankton respectively. The third term represents the organic nitrogen of the grazed but unassimilated phytoplankton. The last two terms represent decomposition, settling, and other effects that contribute to the overall removal of organic nitrogen.

In their study of the Gray's Harbor/Chehalis River, Washington, Battelle (1974) included two nitrogen submodels with different degrees of complexity within their model. One submodel, called the "algal nitrogen" model, incorporates the effects of algae on nitrogen concentrations and is similar to the nitrogen formulations used by Baca and Arnett (1976). The other submodel is a simple first order ammonia-to-nitrate model which can be used when algal effects are not significant.

Tetra Tech (1975, 1976b), Chen and Orlob (1975), and the U.S. Army Corps of Engineers (1974), do not consider a mass balance for organic nitrogen directly in their nitrogen submodels. However, the nitrogenous portion of detritus, which is obtained from the detritus mass balance expression, is considered as a source term for ammonia nitrogen.

Ammonia, another important form of nitrogen, is formed in the aquatic environment from other nitrogen species through several processes. One is nitrogen fixation, a process by which certain bacteria (such as Azotobacter) and blue-green algae convert gaseous nitrogen to inorganic nitrogen, one form of which is ammonia nitrogen. Second, through the process of ammonification or mineralization, wastes containing organic nitrogen are converted by certain organisms to ammonia. Third, denitrification can occur whereby nitrate nitrogen is converted to a more reduced nitrogen form, such as ammonia.

The process of nitrification, which constitutes one of the major sinks of ammonia, refers to the sequential oxidation of ammonia, NH_3, to nitrite, NO_2^-, and finally to nitrate, NO_3^-. As far as is known, only certain autotrophic bacteria are responsible for nitrification. These are Nitrosomonas species for ammonia oxidation and Nitrobacter species for nitrite oxidation:

$$NH_4^+ + 1\tfrac{1}{2}\ O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + 2H^+ + H_2O$$

$$NO_2^- + \tfrac{1}{2}\ O_2 \xrightarrow{\text{Nitrobacter}} NO_3^-$$

The rate of nitrification is primarily dependent on temperature and pH. Wezerak and Gannon (1968) give the optimum temperature as 30°C and the optimum pH as 8.5.

A major difficulty in determining the extent of nitrification in a water body is in verifying the presence of nitrifying bacteria (Lombardo, 1972). Stratton and McCarty (1967), as discussed by Lombardo (1972), have presented a method to describe the nitrification process based on the principles of biological kinetics. They represent the rate of change of nitrifying bacterial mass, M, with the following expression:

$$\partial M/\partial t = -a\ \partial C/\partial t - bM \qquad (2\text{-}78)$$

where $\partial M/\partial t$ = rate of change of bacterial mass, mg/l-hr

C = substrate (NH_3 or NO_2^-) concentration, mg/l

b = organic decay parameters, hr^{-1}; typically 0.002-0.004

M = bacterial mass, mg/l

a = yield constant, mg bacterial mass/mg substrate: (0.29 mg/mg for NH_3 oxidation
0.084 mg/mg for NO_2^- oxidation)

The rate of change of substrate is given by:

$$\partial C/\partial t = -\frac{kMC}{k_m + C} \qquad (2\text{-}79)$$

where k = substrate utilization constant, hr^{-1}: $NH_3 \rightarrow 0.0613$ @ 20°C

$NO_2^- \rightarrow 0.204$ @ 20°C

k_m = half-saturation constants, mg/l: $NH_3 \rightarrow 1.848$

$NO_2^- \rightarrow 0.69$

The use of these Michaelis-Menton type formulations for ammonia and nitrite oxidation includes the effect of bacterial mass on the rate of the nitrification reaction. Hence, knowledge of the bacterial population is necessary if this approach is used. A major difficulty in applying formulations of this type is in obtaining a value for the initial bacterial population.

The nitrification process can also be modeled using several other kinetics formulations. In addition to the Michaelis-Menton type formulation, Huang and Hopson (1974) discuss the zero-order and first-order kinetics assumptions, and autocatalytic growth equation as methods for simulating nitrification. Wezernak and Gannon (1968) use an integrated form of the Robertson growth equation to model instream nitrification. Stratton, et al. (1969) comment on the work of Wezernak and Gannon, and discuss the relative merits of the Robertson, Monod, and zeroth order models. In Section 3.6, a more detailed discussion is given of the single step first-order reaction coefficient.

The effects of the nitrification process are generally considered, in nutrient models, to be part of the source/sink terms for the major inorganic nitrogen forms. Generally, simulation of the inorganic nitrogen forms includes the following processes in addition to the nitrification considerations: 1) BOD degradation (detrital decomposition), 2) algal uptake and respiration, 3) inorganic portion of zooplankton excretion, and 4) bacterial regeneration.

Phytoplankton are known to utilize both ammonia and nitrate for primary production. Models by Thomann, et al. (1974), and Canale, et al. (1976) distinguish between algal utilization of these two nutrients.

Auer (Canale, et al. (1976)) found that the uptake of inorganic nitrogen forms appears to be controlled by complex environmental and intracellular conditions including trace element availability, light and carbon dioxide levels, internal and external pH, and cell age. Auer found some reports of ammonia preference over nitrate, although his review found no consensus on the subject.

Typical formulations for the inorganic nitrogen forms--ammonia, nitrite, and nitrate--as given by Lorenzen, et al. (1974) are:

$$dC_1/dt = -J_1 C_1 - P G_p A_{np} \left(\frac{C_1}{C_1 + C_3} \right) + J_4 C_4 \qquad (2\text{-}80)$$

$$dC_2/dt = J_1 C_1 - J_2 C_2 \qquad (2\text{-}81)$$

$$dC_3/dt = J_2 C_2 - P G_p A_{np} \left(\frac{C_3}{C_1 + C_3} \right) - J_3 C_3 \qquad (2\text{-}82)$$

where C_1 = ammonia nitrogen concentration, mg/l

C_2 = nitrite nitrogen concentration, mg/l

C_3 = nitrate nitrogen concentration, mg/l

J_1 = rate constant for ammonia oxidation, day^{-1}

J_2 = rate constant for nitrite oxidation, day^{-1}

J_3 = denitrification rate constant, day^{-1}

A_{np} = ratio of nitrogen to carbon in algal cells, mg-N/mg-C

J_4 = rate constant for organic nitrogen oxidation, day^{-1}

C_4 = organic nitrogen concentration, mg/l

G_p = net algal growth rate, day^{-1}

P = phytoplankton concentration, mg-C/l

Battelle's Gray's Harbor/Chehalis River model (Battelle, 1974) has expressions for representing the inorganic nitrogen forms in the algal nitrogen model which are identical to the general forms presented above. They also have an alternate ammonia-nitrate model which has the following formulation for the inorganic nitrogen forms:

$$dC_1/dt = -J_2\, C_1 \tag{2-83}$$

$$dC_3/dt = J_2\, C_1 \tag{2-84}$$

where J_2 = rate constant for ammonia oxidation, day^{-1}

Baca and Arnett (1976) use an expression for ammonia that is modified slightly, as compared with Equation (2-80), to include a preference factor for ammonia versus nitrate and an ammonia sediment term, as follows:

$$dC_1/dt = -J_1\, C_1 - P\, G_p\, A_{np}\left(\frac{\gamma C_1}{\gamma C_1 + (1-\gamma)C_3}\right) + J_4\, C_4 + J_5\, C_5 \tag{2-85}$$

where C_5 = sediment nitrogen concentration, mg/l

J_5 = rate of ammonia formation in sediments, day^{-1}; typically 0.01-0.1

γ = preference factor, decimal, unitless

Baca and Arnett's nitrite and nitrate formulations (Baca and Arnett, 1976) are identical to the general formulations given previously except the nitrate formulation contains an uptake preference factor, γ, as used in Equation (2-85) above.

The model of Canale, et al. (1976) considers a one-step nitrification process where ammonia decays directly to nitrate. Their formulation for ammonia is given as:

$$\begin{aligned} dC_1/dt = {} & NCR \cdot (1\text{-}A21) \cdot \sum_z \begin{bmatrix} \text{respiration} \\ \text{loss} \end{bmatrix}_z + A20 \cdot T \cdot ORGN \\ & - A22 \cdot T \cdot C_1 \\ & - NCR \cdot \left(\frac{(ANH_3) \cdot C_1}{ANH_3 \cdot C_1 + (1.\text{-}ANH_3) \cdot C_3} \right) \cdot \sum_p \left[\text{growth} \right]_p \\ & + LOAD_{16} \end{aligned} \qquad (2\text{-}86)$$

where A22 = decay rate of ammonia nitrogen to nitrate, $(\text{day-}°\text{C})^{-1}$

ANH_3 = preference factor, unitless

$LOAD_{16}$ = waste loading rate of ammonia nitrogen, mg/epilimnion 1-day

The first term in the expression refers to the ammonia form of inorganic nitrogen obtained from zooplankton respiration. The second term refers to ammonia received from organic nitrogen decay and the third term is the sink due to ammonia decay to nitrate. The fourth term refers to ammonia loss due to algal uptake. The final term accounts for external sources of ammonia.

The formulation used for the nitrate source/sink expression is given by Canale, et al. (1976) as:

$$\begin{aligned} dC_3/dt = {} & A22 \cdot T \cdot C_1 \\ & - NCR \cdot \left(\frac{(1 - ANH_3) \cdot C_3}{ANH_3 \cdot C_1 + (1\text{-}ANH_3) \cdot C_3} \right) \cdot \sum_p \left[\text{growth} \right]_p \\ & + LOAD_{17} \end{aligned} \qquad (2\text{-}87)$$

where LOAD_{17} = waste loading rate of nitrate nitrogen, mg/epilimnion l-day

The first term in the above equation is the source of nitrate due to ammonia oxidation. The second term considers algal uptake of nitrate and the final term accounts for external inputs.

Canale, et al. (1976) also include a balance expression for "total inaccessible nitrogen," which considers detrital and phytoplankton nitrogen losses to the bottom layers due to settling:

$$\frac{dTIN}{dt} = A23 \cdot SINK(t) \cdot DN \cdot VOLEP^{*} + NCR \cdot \sum_{p} \begin{bmatrix} \text{sinking} \\ \text{loss} \end{bmatrix}_{p} \cdot VOLEP + \left[LOAD_{15} + LOAD_{16} + LOAD_{17} \right] \cdot VOLHY \quad (2\text{-}88)$$

where VOLEP = epilimnion volume, l

VOLHY = hypolimnion volume, l

LOAD = same as defined earlier, except mg/hypolimnion l-day

Thomann, et al. (1974), in a manner similar to Canale, represent the inorganic nitrogen forms as a single step oxidation, considering source/sink formulations for ammonia and nitrate only. For ammonia, C_1, and nitrate, C_3, the source/sink terms are:

$$dC_1/dt = K_o\, C_4 - K_{12}\, C_1 - a_{np} \lambda\, G_p\, P \quad (2\text{-}89)$$

$$dC_3/dt = K_{12}\, C_1 - a_{np}\, (1 - \lambda)\, G_p\, P \quad (2\text{-}90)$$

where K_o = rate of production of ammonia from organic nitrogen, day^{-1}

K_{12} = rate of oxidation of ammonia to nitrate, day^{-1}

λ = preference coefficient, unitless

a_{np} = nitrogen to phytoplankton chlorophyll ratio

If the ammonia is preferentially assimilated by phytoplankton the preference coefficient, λ, is introduced, specifying that ammonia is used until its concentration reaches the range of the inorganic nitrogen half-saturation constant, at which point the nitrogen source shifts to nitrate.

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[*] The factor VOLEP was not included here in the equation in the original reference. However, based upon a personal communication with R.P. Canale (July 14, 1978) TIN is in mass units. Accordingly, volume must multiply every concentration flux term to keep units consistent.

Tetra Tech (1975), Chen and Orlob (1975), and the U.S. Army Corps of Engineers (1974) use a two step oxidation representation for the inorganic nitrogen forms, and include separate source/sink formulations for ammonia, nitrite, and nitrate. The representations proposed for ammonia are similar to the general formulations previously described in most respects. They include a source of ammonia nitrogen from detrital decay, and losses of ammonia due to oxidation to nitrite and preferential algal uptake. In addition to these commonly considered sources and sinks, the nitrogen models of Chen and Orlob (1975) also consider sources of ammonia due to fish and benthic animal respiration. The formulations used by Chen and Orlob for nitrite and nitrate source/sinks are conceptually identical to those given by Baca and Arnett (1976).

Anderson, et al. (1976) represent the inorganic forms of nitrogen with a two step oxidation process, and consider source/sink terms for ammonia, nitrite, and nitrate. Anderson's ammonia formulation neglected algal uptake as a sink of ammonia, considering ammonia oxidation to nitrite as the sole ammonia removal mechanism. The single source of ammonia was considered to be from decaying organic nitrogen. In Anderson's nitrate formulation, nitrate was considered to be utilized exclusively for synthesis reactions and the single source term was considered to be nitrite oxidation to nitrate.

Lombardo (1973) considers the following processes to influence ammonia concentrations: 1) BOD decay, 2) nitrification (either first-order or Michaelis-Menton type reaction as proposed by Stratton and McCarty (1967), both with temperature dependence), 3) algal growth with ammonia used as the sole source of algal nitrogen, and 4) denitrification.

Denitrification is the process by which highly oxidized forms of nitrogen, such as nitrate, are converted to more reduced forms, such as ammonia. Denitrification occurs mostly under anaerobic conditions. It occurs in muds where anaerobic conditions may exist, either below or at the surface layer. Vollenweider (Lombardo, 1972) estimated denitrification rates in some Swiss lakes, with the highest value being 56.5 mg-N/m^2-day. Denitrification has been observed to proceed with traces of oxygen and when dissolved oxygen was as high as 5 ppm (Lombardo, 1972).

Two commonly proposed mechanisms for denitrification are:

$$HNO_3 \rightarrow HNO_2 \rightarrow H_2N_2O_2 \rightarrow NH_2OH \rightarrow NH_3$$

and

$$2NO_3^- \rightarrow N_2 + H_2O + \frac{5}{2} O_2$$

The important difference between these two possible reaction mechanisms is that in the first expression, nitrate is reduced to soluble and readily oxidizable ammonia, while in the second it is reduced to gaseous nitrogen and eventually escapes the aquatic system. Lombardo (1972), in discussing the nitrogen balance in lakes, stated that it is safe to assume that the gaseous nitrogen end product predominates from the quantitative standpoint.

In his Delaware Estuary model, Kelly (1975) initially considered only total kjeldahl nitrogen (organic plus ammonia nitrogen) in his nitrogen formulation. However, early runs of the model indicated that the conversion of organic nitrogen and ammonia nitrogen to other forms in the estuary had to be included in the simulation. When the conversion of ammonia to nitrate, as a function of temperature and dissolved oxygen and toxic substances concentrations, was included in the model, it caused the model to behave more realistically with respect to nitrogen concentrations measured in the estuary.

Table 2-16 presents a listing of coefficient values commonly used in nitrogen formulations. Decay rates, reported at 20°C unless otherwise noted, are temperature dependent. They are usually adjusted with the following temperature correction expression:

$$k_T = k_{20}\ \theta^{(T-20)} \tag{2-91}$$

where k_T = rate at T°C

k_{20} = rate at 20°C

θ = temperature coefficient

The utilization of oxygen by nitrification is an area of concern in many water quality models since a sufficient oxygen content in a water system is crucial to most biota. The usual procedure in water quality models is to use the N:O stoichiometric equivalence which can be combined with a sink term in the dissolved oxygen mass balance formulation (e.g., see Chen and Orlob, 1975). This stoichiometric equivalence gives an estimate of the amount of oxygen utilized in oxidizing a specific amount of nitrogen.

Values of stoichiometric equivalence will vary depending on the form of nitrogen being converted. The oxidation of ammonia to nitrite requires 3.43 grams of oxygen for one gram of nitrogen oxidized to nitrite. The reaction which completes the oxidation requires 1.14 grams of oxygen per gram of nitrite oxidized to nitrate. Therefore the total dissolved oxygen utilization in the entire nitrification process is 4.47 grams of oxygen per gram of ammonia oxidized to nitrate.

Lombardo (1972) reports, however, that due to fixation of carbon dioxide by bacteria, oxygen utilization is generally less than these theoretical values. Wezernak and Gannon (1968) suggest values of 3.22 gram of oxygen per gram of ammonia oxidized to nitrite and 1.11 gram oxygen per gram nitrite oxidized to nitrate.

TABLE 2-16. VALUES FOR COEFFICIENTS IN NITROGEN FORMULATIONS

Organic (Detrital) Nitrogen Decay Rate (day^{-1})	Ammonia Nitrogen Decay Rate to NO_3 (day^{-1})	Ammonia Nitrogen Decay Rate to NO_2 (day^{-1})	Nitrite Nitrogen Decay Rate to NO_3 (day^{-1})	Organic (Detrital) Nitrogen Settling Rate (day^{-1})	Location of Study	Reference
0.02-0.4	-	0.1-0.5	3.0-10.0	-	-	Baca and Arnett (1976)
0.005	-	0.10	0.5	-	N. Fork Kings River, California	Tetra Tech (1976b)
0.001-0.02	-	0.05-0.02	0.2-0.5	-	-	U.S. Army Corps of Engineers (1974)
-	-	0.03	0.09	-	Lake Washington	Chen and Orlob (1975)
0.024	0.16	-	-	0.05	Lake Michigan	Canale, et al. (1976)
-	-	-	-	-	San Joaquin River, California	O'Connor, et al. (1975)
-	-	-	-	-	San Joaquin River Estuary, California	O'Connor, et al. (1975)
0.14	0.2	-	-	0.10	Potomac Estuary	O'Connor, et al. (1975)
0.04	0.052	-	-	0.028	Lake Erie	O'Connor, et al. (1975)
0.035	0.04	-	-	0.001	Lake Ontario	O'Connor, et al. (1975)
-	-	0.1	0.3	-	Boise River, Idaho	Chen and Wells (1975)
-	-	0.003	0.009	-	San Francisco Bay Estuary	Chen (1970)
0.1-0.4	-	0.1-0.5	5.0-10.0	-	Gray's Harbor/ Chehalis River, Washington	Battelle (1974)

(continued)

TABLE 2-16. (continued)

Denitrification Rate (day^{-1})	N to C Ratio for Zooplankton (mg-N/mg-C)	N to C Ratio for Phytoplankton (mg-N/mg-C)	N to Chlor Ratio for Phytoplankton	Location of Study	Reference
0.0-1.0	0.05-0.17	0.05-0.17	-	-	Baca and Arnett (1976)
-	-	-	-	N. Fork Kings River, California	Tetra Tech (1976b)
-	-	-	-	-	U.S. Army Corps of Engineers (1974)
-	-	-	-	Lake Washington	Chen and Orlob (1975)
-	0.2	0.2	-	Lake Michigan	Canale, *et al*. (1976)
-	0.14	0.14	7	San Joaquin River, California	O'Connor, *et al*. (1975)
-	0.14	0.14	7	San Joaquin River Estuary, California	O'Connor, *et al*. (1975)
-	0.2	0.2	10	Potomac Estuary	O'Connor, *et al*. (1975)
-	7/50	7/50	7	Lake Erie	O'Connor, *et al*. (1975)
-	0.2	0.2	10	Lake Ontario	O'Connor, *et al*. (1975)
-	-	-	-	Boise River, Idaho	Chen and Wells (1975)
-	-	-	-	San Francisco Bay Estuary	Chen (1970)
-	-	0.17	-	Gray's Harbor/ Chehalis River, Washington	Battelle (1974)

2.5.2 Phosphorus Cycle

The phosphorus cycle operates like the nitrogen cycle in many respects. Organic forms of phosphorus are generated by the death of phytoplankton and zooplankton. Therefore, organic phosphorus, like organic nitrogen, is often present as detritus. Generally phosphorus in this form is assumed to be converted to the inorganic state in which form it is available to algae for primary production. Figure 2-14 shows phosphorus cycle pathways. With the exception of sediment exchange, the pathways shown are those of major importance.

Most model representations of the phosphorus systems consider both organic and inorganic fractions. Occasionally a separate formulation for sediment phosphorus is also included. The usual procedure in water quality models, as with the nitrogen system, is to formulate source/sink terms for these phosphorus groups. The source/sink terms are then included in complete mass balance expressions, which also include expressions for the transport of the various suspended or dissolved phosphorus forms by advection and diffusion.

The internal processes which are generally assumed to affect the concentrations of the various phosphorus forms are: 1) algal uptake and release, 2) zooplankton release, 3) detrital decay, 4) loss to sediments (through adsorption, precipitation, and/or settling), 5) bacterial regeneration, and 6) benthal deposits release. A set of formulations which represents the phosphorus system is given as (Lorenzen, et al., 1974):

$$dD_1/dt = -G_p \, P \, A_{pp} + I_2 \, D_2 - I_1 \, D_1 + I_3 \, D_3 \qquad (2\text{-}92)$$

$$dD_3/dt = D_p \, P \, A_{pp} + D_z \, Z \, A_{pz} - I_1 \, D_3 - I_3 \, D_3 \qquad (2\text{-}93)$$

and if sediment phosphorus is considered:

$$dD_2/dt = I_1 \, D_1 - I_2 \, D_2 \, (+ \, I_1 \, D_3)^* \qquad (2\text{-}94)$$

where D_1 = soluble inorganic phosphorus, mg/l

D_2 = total sediment phosphorus, mg/l

D_3 = organic phosphorus in water column, mg/l

P = phytoplankton carbon concentration, mg/l

Z = zooplankton carbon concentration, mg/l

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*Note that in Lorenzen, et al. (1974), due to an oversight (Lorenzen, M.W., pers. comm., July 10, 1978), the term "+ I_1 D_3" was not included.

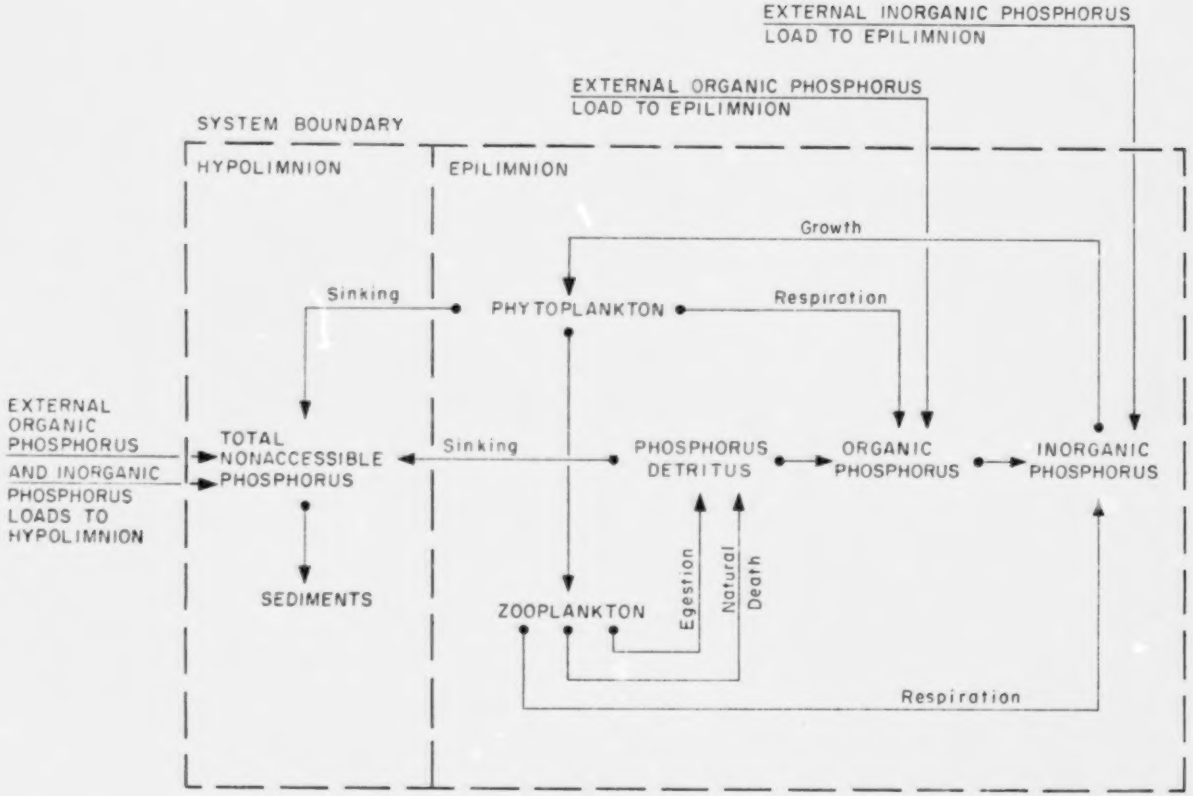

EXTERNAL INORGANIC PHOSPHORUS
LOAD TO EPILIMNION
EXTERNAL ORGANIC PHOSPHORUS
LOAD TO EPILIMNION
SYSTEM BOUNDARY
HYPOLIMNION
EPILIMNION
Growth
Sinking
PHYTOPLANKTON
Respiration
EXTERNAL ORGANIC PHOSPHORUS
AND INORGANIC PHOSPHORUS LOADS TO HYPOLIMNION
TOTAL NONACCESSIBLE PHOSPHORUS
Sinking
PHOSPHORUS DETRITUS
ORGANIC PHOSPHORUS
INORGANIC PHOSPHORUS
SEDIMENTS
ZOOPLANKTON
Egestion
Natural Death
Respiration

Figure 2-14. Pathways used in modeling the phosphorus cycle in Lake Michigan (modified after Canale, et al., 1976).

A_{pp} = phosphorus to carbon ratio in phytoplankton, mg/mg

A_{pz} = phosphorus to carbon ratio in zooplankton, mg/mg

I_1 = rate constant for loss to sediments by sorption, precipitation, day^{-1}

I_2 = sediment release (desorption, solvation) rate constant, day^{-1}

I_3 = rate constant for release of soluble inorganic phosphorus from organic phosphorus, day^{-1}

D_p = specific death rate of phytoplankton, day^{-1}

D_z = specific death rate of zooplankton, day^{-1}

G_p = specific growth rate of algae, day^{-1}

Lorenzen, et al. (1974) assumes that the rate of loss of water column organic phosphorus to the sediment (I_1) is the same as the rate of loss of soluble inorganic phosphorus to the sediment. Figure 2-15 shows schematically the pathways in this model.

Baca and Arnett (1976) use nearly identical formulations in their model for the phosphorus cycle as those given above. Expressions for organic phosphorus and inorganic phosphorus are essentially the same, but their expression for sediment phosphorus is slightly different. In Baca and Arnett's formulation a distinct rate constant (I_4) is used for loss of organic phosphorus to the sediment.

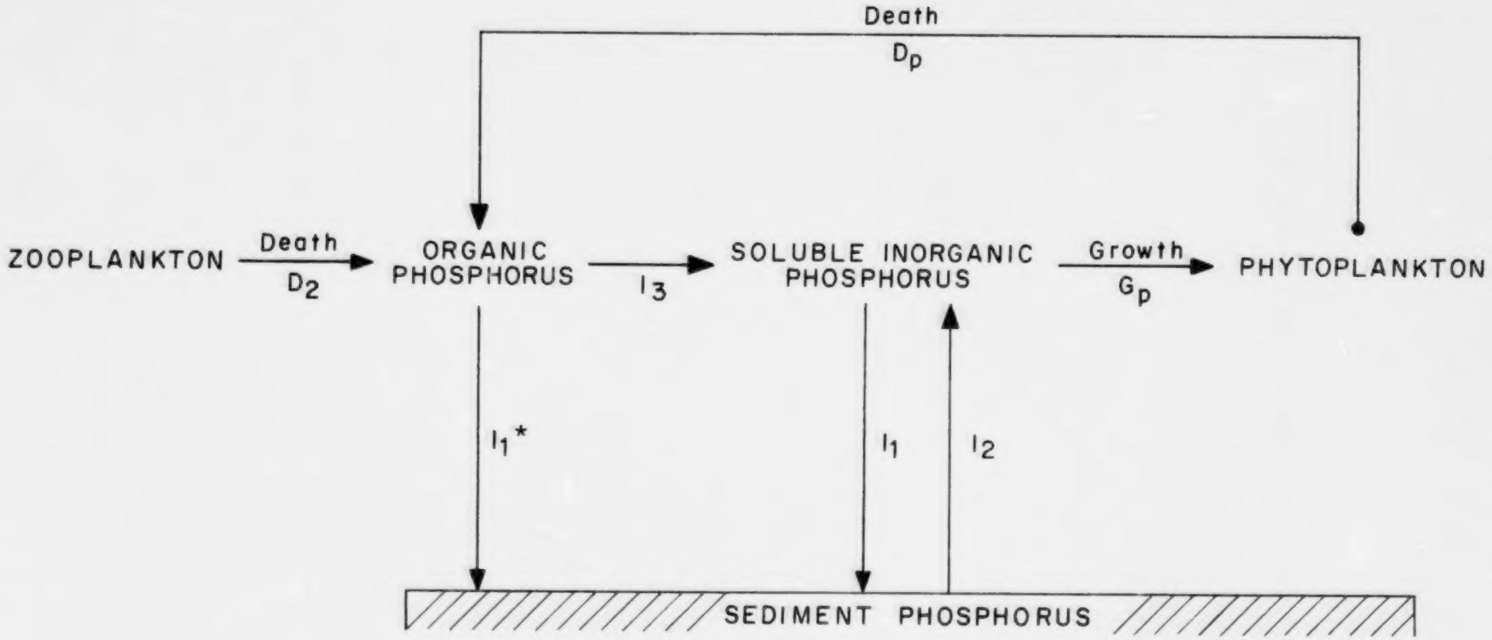
$$dD_2/dt = I_1 D_1 + I_4 D_3 - I_2 D_2 \qquad (2\text{-}95)$$

where I_4 = rate of organic phosphorus loss to sediments, day^{-1}; typically 0.01-0.03

I_2 = rate constant for sediment release of inorganic phosphorus, day^{-1}; typically 0.1-0.7

I_1 = rate constant for loss of soluble phosphorus to sediments, day^{-1}; typically 0.1-0.7

O'Connor, Di Toro, and Thomann (1975) use the following formulations for simulating the phosphorus system. The formulations are analogous to their expressions representing nitrogen kinetics:


Death
D_p
ZOOPLANKTON
Death
D_2
ORGANIC PHOSPHORUS
I_3
SOLUBLE INORGANIC PHOSPHORUS
Growth
G_p
PHYTOPLANKTON
I_1*
I_1
I_2
SEDIMENT PHOSPHORUS

*This pathway was not included in Equation (2-94) as shown in the original reference.

Figure 2-15. Pathways of phosphorus in the model by Lorenzen, et al. (1974).

$$\frac{dD_3}{dt} = a_{pp}\, D_p\, P + \frac{a_{pp}}{a_{zp}}\, D_z\, Z + \frac{a_{pp}}{a_c}\, P \left[1 - \frac{a_{zp}\, K_{mp}}{K_{mp} + P} \right] C_g\, Z - K_o\, D_3 - K_s\, D_3 \qquad (2\text{-}96)$$

where D_3 = organic phosphorus concentration, mg-P/l

a_{pp} = phosphorus to chlorophyll ratio, mg P/mg Chl

a_c = carbon to chlorophyll ratio, mg C/mg Chl in zooplankton excreta

a_{zp} = carbon to chlorophyll ratio, mg C/mg Chl in zooplankton biomass

D_p = specific death rate for phytoplankton, day^{-1}

D_z = specific death rate for zooplankton, day^{-1}

P = phytoplankton chlorophyll concentration in the water column, mg/l

Z = zooplankton chlorophyll concentration in the water column, mg/l

K_{mp} = half-saturation constant for zooplankton grazing, mg/l

C_g = zooplankton grazing rate, $\text{day}^{-1}\ (\text{mg/l})^{-1}$

K_o = decay rate of organic phosphorus to inorganic phosphorus, day^{-1}

K_s = settling removal or additional decay rate to inorganic forms, day^{-1}

The first and second terms in the above expression represent contributions to the organic phosphorus concentration due to phytoplankton and zooplankton composite death and respiration, respectively. The third term represents a source of organic phosphorus due to zooplankton excretions. In the model, phytoplankton are assumed to provide all zooplankton excretion organic phosphorus. The fourth term is a loss of organic phosphorus due to first order decay and the last term is any additional decay or settling removal of organic phosphorus.

For inorganic phosphorus, which is assumed to be available to the phytoplankton for assimilation, the equation is:

$$dD_1/dt = K_0 \; D_3 - a_{pp} \; G_p \; P - K_1 \; D_1 \qquad (2\text{-}97)$$

where G_p = phytoplankton specific growth rate, day^{-1}

K_1 = rate constant for loss of inorganic phosphorus other than to phytoplankton growth, day^{-1}

The first term represents a source of inorganic phosphorus due to organic phosphorus decay. The second and third terms are losses due to algal uptake and settling (or additional decay), respectively.

The phosphorus representation used by Thomann, et al. (1975) differs from that of Lorenzen, et al. (1974) and that used by Baca and Arnett (1976) in two respects. First, sediment phosphorus is not considered in a separate expression, although settling terms are included in the above two equations. Second, an additional term for contributions to the organic phosphorus concentration due to zooplankton excretions is included in the Thomann formulation.

The representation of the phosphorus system used by Canale, et al. (1976) in their water quality model is analogous to their nitrogen system representation. The phosphorus cycle submodel considers detrital phosphorus and organic phosphorus as separate constituents (see Figure 2-14). As in the nitrogen representation, the phosphorus detritus is considered to be removed from the system by both settling and decay to dissolved organic phosphorus. Canale reports that the reaction rates governing detrital-to-organic phosphorus transfer and organic-to-inorganic phosphorus transfer far exceed the fastest biological rates observed in the system.

The detrital phosphorus equation, as given by Canale, et al., is as follows:

$$\begin{aligned} dDetP/dt = {} & PCR \cdot \sum_z \left(\left(1 - \begin{bmatrix} \text{assimilation} \\ \text{efficiency} \end{bmatrix}_z \right) \cdot \begin{bmatrix} \text{eating} \\ \text{rate} \end{bmatrix}_z \cdot ZOO_z \right) \\ & + PCR \cdot \sum_z \left(\begin{bmatrix} \text{natural} \\ \text{death} \end{bmatrix}_z \right) - A17 \cdot T \cdot DetP \qquad (2\text{-}98) \\ & - A23 \cdot SINK(t) \cdot DetP \end{aligned}$$

where PCR = phosphorus to carbon ratio, in detritus, mg P/mg C; typically 0.2

A17 = detrital phosphorus to dissolved organic phosphorus decay rate, $(\text{day} - {}^\circ\text{C})^{-1}$; typically 0.01

A23 = maximal detrital sinking rate, day^{-1}

ZOO = zooplankton concentration, mg/l

T = temperature, °C

DetP = detrital phosphorus concentration, mg/l

Sink(t) = seasonal correction for sinking rate, unitless

For the dissolved organic phosphorus concentration, Canale, et al. (1976) propose the following expression:

$$\begin{aligned} dDisP/dt = {} & PCR \cdot \sum_p \begin{bmatrix} \text{respiration} \\ \text{loss} \end{bmatrix}_p + A17 \cdot T \cdot DetP \\ & - A19 \cdot T \cdot DisP + LOAD_{19} \end{aligned} \tag{2-99}$$

where A19 = organic phosphorus to inorganic phosphorus decay rate, $(\text{day} - °\text{C})^{-1}$

DisP = dissolved organic phosphorus concentration, mg/l

$LOAD_{19}$ = external dissolved organic phosphorus loading, mg/epilimnion l-day

Canale's representation of the total organic phosphorus with two separate formulations, namely detrital phosphorus and dissolved organic phosphorus, enables contributions from the various algal and zooplankton sources to be entered into the system in one of two possible forms, with each form displaying a different decay characteristic. By separating the organic forms, Canale's more complex formulation attempts to simulate the decay of the various phosphorus forms more exactly.

Canale's formulation for the dissolved inorganic phosphorus concentration is given as:

$$\begin{aligned} dInorgP/dt = {} & PCR \cdot \sum_z \begin{bmatrix} \text{respiration} \\ \text{loss} \end{bmatrix}_z + A19 \cdot T \cdot DisP \\ & - PCR \cdot \sum_p \begin{bmatrix} \text{growth} \end{bmatrix}_p + LOAD_{20} \end{aligned} \tag{2-100}$$

where InorgP = dissolved inorganic phosphorus concentration, mg/l

$LOAD_{20}$ = external dissolved inorganic phosphorus loading, mg/epilimnion l-day

In addition to the above expressions, Canale, et al. (1976) also includes a source/sink formulation for total nonaccessible phosphorus. This formulation is somewhat analogous to the sediment phosphorus expressions as presented previously in Equations (2-94) and (2-95) with the exception that phosphorus release from the sediments is not considered. Canale's total nonaccessible phosphorus formulation is given as:

$$dNonP/dt = A23 \cdot SINK(t) \cdot DetP \cdot VOLEP^{*} + PCR \cdot \sum_{p} \begin{bmatrix} \text{sinking} \\ \text{loss} \end{bmatrix}_{p} \cdot VOLEP + \left[LOAD_{19} + LOAD_{20}\right] \cdot VOLHY \qquad (2\text{-}101)$$

where NonP = nonaccessible phosphorus, mg

LOAD = same as above but mg/hypolimnion l-day

Lam and Jacquet (1976) have also recognized a need to distinguish between processes involving particulate phosphorus and soluble phosphorus. They consider the following processes to be of fundamental importance in modeling the phosphorus system: 1) the advective and diffusive processes which are primarily responsible for horizontal movement of both soluble and particulate phosphorus; 2) the phenomenon of downward settling of particulate phosphorus; and 3) the regeneration of soluble and particulate phosphorus from sediments due to biological, chemical, and physical causes.

Superimposed on these individual mechanisms are the conversions of phosphorus from one form to another and the interrelations of each form with other water quality parameters. Lam and Jacquet's representation of the phosphorus cycle concentrates on accurately describing the physical phenomena, and sacrifices some detailed representation of biological processes and constituent interactions.

Their formulations for the phosphorus system include mass balance expressions for total phosphorus and particulate phosphorus. The total phosphorus formulation considers settling, regeneration flux of phosphorus from the sediment, and external inputs, in addition to advective and diffusive transports. The particulate phosphorus mass balance formulation, in addition to including the terms considered for the total phosphorus formation, also includes separate terms for soluble phosphorus conversion to particulate phosphorus due to photosynthesis and particulate phosphorus conversion to soluble phosphorus due to respiration.

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*The factor VOLEP was not included here in the original reference. However, based upon a personal communication with R.P. Canale (July 14, 1978) NonP is in units of mass. Accordingly, volume must multiply every concentration flux term to keep units consistent.

Tetra Tech (1975), Chen and Orlob (1975), and the U.S. Army Corps of Engineers (1974), consider a single mass balance formulation for their phosphorus systems. Opinions in the literature differ as to which forms of phosphorus are available to phytoplankton for uptake. Chen and Orlob assume that all dissolved phosphorus forms are available for uptake. Their single mass balance expression for total dissolved phosphorus is given as follows:

$$dTDP/dt = KDET \cdot SD \cdot DP + KB \cdot \Big[ZP \cdot ZR \cdot Z + FP \cdot FR \cdot F + BP \cdot BR \cdot B + PP \cdot (PR - PG) \cdot P\Big] \tag{2-102}$$

where TDP = total dissolved phosphorus concentration, mg/l

KDET = detritus decay rate @ local temperature, day^{-1}

SD = effective detritus concentration = detritus concentration + equivalent concentration, mg/l

DP = phosphorus portion of detritus, unitless

KB = biota activity rate coefficient, unitless

ZP = phosphorus portion of zooplankton, unitless

Z = zooplankton concentration, mg/l

ZR = zooplankton respiration rate at 20°C, day^{-1}

FP = phosphorus portion of fish, unitless

FR = fish respiration rate @20°C, day^{-1}

F = fish concentration, mg/l

BP = phosphorus portion of benthic animal population, unitless

BR = benthic animal respiration rate, day^{-1}

B = benthic animal concentration, mg/l

PP = phosphorus portion of phytoplankton, unitless

PR = phytoplankton respiration rate, day^{-1}

PG = phytoplankton specific growth rate, day^{-1}

P = phytoplankton concentration, mg/l

In the above expression, particulate phosphorus in the form of detrital phosphorus, is assumed to decay to a dissolved form, thus contributing to the dissolved phosphorus concentration.

Sediment phosphorus is not represented in a separate expression by Chen and Orlob, in contrast to the representation suggested by Baca and Arnett (1976). In Tetra Tech's phosphorus system modeling approach (Tetra Tech, 1975) the sediment contributions are not specifically formulated in the mass balance expression. Sediment contributions are included indirectly, however, by considering the phosphorus portion of respired benthic algae to be a source of dissolved phosphorus. Tetra Tech considers detrital settling in the mass balance expression for detritus which in effect accounts for particulate phosphorus settling. A separate settling term is not included in the phosphorus mass balance.

Lombardo (1973) considers two groups of phosphorus in his submodel on orthophosphate and potential phosphorus. Orthophosphate concentrations are determined as a function of the following processes: 1) BOD decay, 2) algal growth and respiration, 3) zooplankton excretion, and 4) benthic deposits release. The other phosphorus form, "potential phosphorus" defined as that portion of phosphorus which is degradable to orthophosphate, is assumed to be controlled by the following: 1) BOD changes, 2) phytoplankton and zooplankton population changes, and 3) zooplankton excretion.

As in their nitrogen submodel, Battelle (1974) offers a choice of submodels for the phosphorus system. For the phosphorus system, three different models are available: 1) an algal phosphorus model, 2) a first order phosphorus model, and 3) a second order phosphorus model. The first order model assumes that only reactions between soluble and sediment phosphorus occur. This model uses the following equations:

$$dD_1/dt = -I_1 D_1 + I_2 D_2 \tag{2-103}$$

$$dD_2/dt = -I_2 D_2 + I_1 D_1 \tag{2-104}$$

where I_1 = decay rate for sediment phosphorus to soluble phosphorus, day^{-1}

I_2 = decay rate for soluble phosphorus to sediment phosphorus, day^{-1}

D_1 = sediment phosphorus concentration, mg/l

D_2 = soluble phosphorus concentration, mg/l

The second order model uses the following single expression:

$$dD_1/dt = -I_1 D_1^2 \tag{2-105}$$

Sediment exchange is not considered in the second order model.

The algal phosphorus model is similar to that of Lorenzen, et al. (1974) for the phosphorus system and to that of Baca and Arnett (1976) as discussed previously. Battelle's algal model assumes that the reactions between the various forms of phosphorus can be described by a first order relationship.

O'Melia (1974) has also developed a lake phosphorus model that has a stratification period lasting six months. The lake is then assumed to be unstratified the other six months of the year. A two box model is used for the summer period (with the epilimnion and hypolimnion comprising each box). Both boxes are well-mixed. Two phosphorus compartments, soluble orthophosphate and particulate phosphorus, are used for each of the boxes. The two compartment assumption was found useful for modeling phosphorus over a time period of months and seasons.

For the summer model, four interdependent linear differential equations are needed for mass balances of orthophosphate and particulate phosphorus in the two boxes, while in the winter only two differential equations are needed for the single box. Phosphorus inputs from the sediment are not considered.

Table 2-17 presents a listing of commonly used coefficient values for phosphorus formulations. The decay rates, reported at 20°C, are generally temperature dependent, and can be adjusted with the same temperature correction expression as used for the nitrogen rates.

2.5.3 Silicate Cycle

Since green algae, blue-green algae, and zooplankton require only trace amounts of silicon, the silicon cycle is usually considered to involve only the diatoms, particulate (detrital) silicon forms, and dissolved silicate. Diatoms, unlike other commonly considered phytoplankton groups, require the element silicon for continued production. A typical representation of the silicon cycle, as given by Canale, et al. (1976), is shown in Figure 2-16. Because the presence of silicon is very rarely a dominating factor and is limited to such a restricted area of concern, it is generally simulated only in models of considerable complexity.

Canale, et al. (1976) consider three forms of silicon in their representation: detrital silicon, dissolved silicon, and total nonaccessible silicon. The mathematical formulations for these three forms are given as:

$$\frac{dDETSIL}{dt} = SCR \cdot \sum_{\text{diatoms}} \left(\begin{bmatrix} \text{respiration} \\ \text{loss} \end{bmatrix}_p + \begin{bmatrix} \text{predation} \\ \text{loss} \end{bmatrix}_p \right) \qquad (2\text{-}106)$$

$$- A16 \cdot T \cdot DETSIL - A23 \cdot SINK(t) \cdot DETSIL$$

TABLE 2-17. VALUES FOR COEFFICIENTS IN PHOSPHORUS FORMULATIONS

Organic Phosphorus Decay Rate (day^{-1})	Detrital Phosphorus Decay Rate to Dissolved Form (day^{-1})	Detrital (Particulate) Settling Rate (day^{-1})	Phosphorus to Carbon Ratio for Zooplankton	Phosphorus to Carbon Ratio for Phytoplankton	Phosphorus to Chlorophyll Ratio	Location of Study	Reference
0.1-0.7	-	0.01-0.1	0.024-0.24	0.024-0.24	-	-	Baca and Arnett (1976)
-	0.005	-	-	-	-	N. Fork Kings River, California	Tetra Tech (1976b)
0.14	-	0.10	-	-	1	Potomac Estuary	O'Connor, et al. (1975)
0.40	-	0.028	-	-	1	Lake Erie	O'Connor, et al. (1975)
0.14	-	0.001	-	-	1	Lake Ontario	O'Connor, et al. (1975)
-	0.001-0.02	-	-	-	-	-	U.S. Army Corps of Engineers (1974)
0.20	0.20	0.05	0.2	0.2	-	Lake Michigan	Canale, et al. (1976)
0.1-0.7	-	-	-	-	-	-	Battelle (1974)

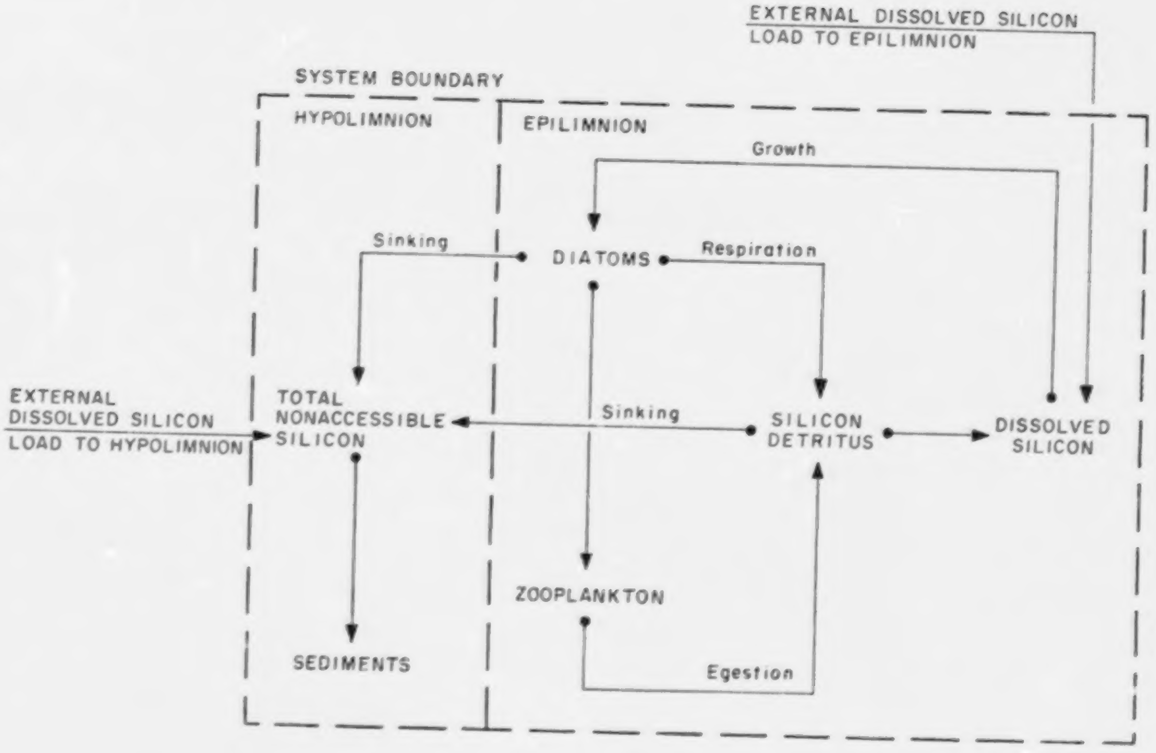
EXTERNAL DISSOLVED SILICON
LOAD TO EPILIMNION
SYSTEM BOUNDARY
HYPOLIMNION
EPILIMNION
Growth
Sinking
DIATOMS
Respiration
EXTERNAL
DISSOLVED SILICON
LOAD TO HYPOLIMNION
TOTAL
NONACCESSIBLE
SILICON
Sinking
SILICON
DETRITUS
DISSOLVED
SILICON
ZOOPLANKTON
SEDIMENTS
Egestion

Figure 2-16. Pathways used in modeling the silicate cycle (modified after Canale, et al., 1976).

$$\frac{dDISSIL}{dt} = A16 \cdot T \cdot DETSIL - SCR \cdot \sum_{\text{diatoms}} \left[\text{growth}\right]_p + LOAD_{22} \quad (2\text{-}107)$$

$$\frac{dNONSIL}{dt} = A23 \cdot SINK(t) \cdot DETSIL \cdot VOLEP^{*} + SCR \cdot \sum_{\text{diatoms}} \left[\begin{matrix}\text{sinking} \\ \text{loss}\end{matrix}\right]_p \cdot VOLEP + LOAD_{22} \cdot VOLHY \quad (2\text{-}108)$$

where SCR = silicon to carbon ratio, unitless; typically 0.2

A16 = decay rate for detrital silicon to dissolved silicon, (day - °C)$^{-1}$; typically 0.0015

A23 = maximum detrital sinking rate, day^{-1}; typically 0.05

T = temperature, °C

DETSIL = detrital silicon concentration, mg/l

DISSIL = dissolved silicon concentration, mg/l

NONSIL = total nonaccessible silicon, mg

VOLEP = epilimnion volume, l

VOLHY = hypolimnion volume, l

$LOAD_{22}$ = loading rate of dissolved silicon, mg/epilimnion l-day (Eq. (2-107)) and mg/hypolimnion l-day (Eq. (2-108))

It should be noted that the silicon model of Canale, et al. (1976) is coupled with their phytoplankton model, and that in order to simulate silicon, diatoms must be among the modeled phytoplankton species.

Bierman (1976) considered the following mass balance formulation for the dissolved silicon concentration in his model:

$$\frac{dSCM}{dt} = Q/V \left(SCMBD - SCM \right) - \sum_{\text{diatoms}} \left[A(L) \cdot SPGR(L) \cdot SSA(L) \right] + RDCMP \cdot T \cdot TOS + WSCM/V \quad (2\text{-}109)$$

---

[*] Note that VOLEP was not included here in the original reference. Through a personal communication with Canale (July 14, 1978) it was determined that NONSIL is in mass units. In order to make units correct, equation (2-108) has been changed accordingly.

where SCM = silicon concentration in solution, moles/l

SCMBD = boundary value of SCM, moles/l

A(L) = diatom concentration, mg dry wt/l

SPGR(L) = diatom specific growth rate, day^{-1}

SSA(L) = silicon stoichiometry for diatoms (moles/mg dry wt)

RDCMP = decomposition rate from unavailable to available nutrient pool (day - °C)$^{-1}$

TOS = concentration of unavailable silicon, moles/l

T = temperature, °C

WSCM = external point loading rates of available silicon, moles/day

V = system volume

Q = water circulation rate, volume/day

Although silicon representation has generally not been considered by Thomann, O'Connor, and Di Toro in their previous modeling efforts, work is under way to include simulation of the nutrient silicon in their Lake Ontario model (O'Connor, et al. (1975)). Under peak growing conditions in Lake Ontario, surface silica values are about 0.1-0.2 mg Si/l. At the lower concentration levels, the silicon nutrient could be of importance (Thomann, et al., 1975).

2.5.4 Dissolved Oxygen

The oxygen balance in an aquatic ecosystem depends on the capacity of the system to reaerate itself, which is a function of the advection and diffusion processes occurring within the system, and the internal sources and sinks of oxygen. The major sources of oxygen, in addition to atmospheric reaeration, are photosynthetic oxygen production and the oxygen contained in incoming flow. The sinks of dissolved oxygen include biochemical oxidation of carbonaceous and nitrogenous organic matter, benthal oxygen demand, and the oxygen demand of respiring organisms. Available oxygen, therefore, is required for many of the chemical and biological reactions occurring in the ecosystem.

The complete dissolved oxygen mass balance equation involves two basic components: 1) the mass transport portion involving advective and diffusive processes, and 2) a source/sink expression for the individual reactive constituents formulated in a linear fashion. The assertion that dissolved oxygen concentration is a function of reaeration and BOD decay alone has, in many instances, been shown to be an inadequate approach for modeling D.O. fluctuations (see Lombardo (1973) for a discussion of several cases).

A typical source/sink formulation for dissolved oxygen used in current water quality models, as given by Baca and Arnett (1976), is:

$$\frac{dDO}{dt} = \underbrace{K_1 L}_{\text{Carbonaceous BOD}} - \underbrace{\alpha_1 J_1 C_1}_{\text{Ammonia Oxidation}} - \underbrace{\alpha_2 J_3 C_2}_{\text{Nitrite Oxidation}} - \underbrace{\frac{L_b}{\Delta Z}}_{\text{Benthic Uptake}} + \underbrace{K_r\left(DO_s - DO\right)}_{\text{Reaeration}} + \underbrace{\alpha_3\left(G_p - D_p\right)}_{\text{Algal Productivity}} P \tag{2-110}$$

where DO = dissolved oxygen concentration, mg/l

DO_s = dissolved oxygen saturation concentration, mg/l

C_1 = ammonia concentration, mg/l

C_2 = nitrite concentration, mg/l

L = carbonaceous BOD, mg/l

L_b = benthic O_2 uptake rate, g/m^2-day

P = phytoplankton concentration, mg-C/l

G_p, D_p = phytoplankton specific growth and death rates, day^{-1}

P = phytoplankton concentration, mg/l

$\alpha_1, \alpha_2, \alpha_3$ = stoichiometric constants, unitless

K_1, J_1, J_3 = deoxygenation rates, day^{-1}

K_r = reaeration coefficient, day^{-1}

ΔZ = bottom layer thickness, m

The saturated oxygen concentration, DO_S, is mainly a function of temperature, and to a lesser degree, a function of salinity and barometric pressure. It is usually sufficient to obtain the saturated oxygen values by means of an empirical formulation. Expressions for obtaining dissolved oxygen saturation are discussed in Section 3.3.

Table 2-18 presents a listing of the various stoichiometric equivalence values used in dissolved oxygen formulations. The various substrate decay rates, usually converted to an oxygen demand by means of these stoichiometric equivalence values, are more fully discussed in the various sections dealing with the particular substrate processes. Values for these decay rates are reported in the appropriate sections and are not duplicated here.

TABLE 2-18. VALUES FOR STOICHIOMETRIC EQUIVALENCE FOR DISSOLVED OXYGEN FORMULATIONS

Stoichiometric Equivalence	Value	Reference
O_2/NH_4	3.0-3.43	Baca and Arnett (1976)
O_2/NH_3	3.5	Tetra Tech (1976b)
O_2/NH_3	3.5	U.S. Army Corps of Engineers (1974)
O_2/NH_3	3.5	Chen and Wells (1975)
O_2/NH_3	3.5	Chen (1970)
O_2/NO_2	1.5	Chen (1970)
O_2/NO_2	1.2	Chen and Wells (1975)
O_2/NO_2	1.0-1.14	Baca and Arnett (1976)
O_2/NO_2	1.2	Tetra Tech (1976b)
O_2/NO_2	1.2	U.S. Army Corps of Engineers (1974)
O_2/Algae	1.6-2.66	Baca and Arnett (1976)
O_2/Algae	1.6	U.S. Army Corps of Engineers (1974)
O_2/Algae	1.6	Chen and Wells (1975)
O_2/Algae	1.6	Chen (1970)
O_2/Detritus	1.2	Tetra Tech (1976b)
O_2/Detritus	2.0	Chen (1970)
O_2/Detritus	2.0	Chen and Wells (1975)
CO_2/BOD	0.2	Chen and Orlob (1975)

Several investigators have proposed modifications to Baca and Arnett's (1976) basic dissolved oxygen formulation. Formulations for dissolved oxygen balance due to Tetra Tech (1975), the U.S. Army Corps of Engineers (1974), and Chen and Wells (1975) differ from Baca and Arnett's general expression in that they include additional sink terms for the respiration of fish and zooplankton and a term for detritus decay. Lombardo (1973) includes a source term for contributions from the denitrification process. Anderson, et al. (1976) consider the production of dissolved oxygen due to photosynthesis to be contributed by two separate sources: 1) the phytoplankton population, and 2) the attached algae concentration. They propose the following formulation for determining the O_2 production (SOURCE, mg/l-day) by algae:

$$\text{SOURCE} = K_a \left(A_1 + A_2 \right) \qquad (2\text{-}111)$$

where K_a = average rate coefficient of oxygen production by algae, day^{-1}

A_1 = phytoplankton concentration as chlorophyll-a, mg/l

A_2 = attached algae concentration as chlorophyll-a, mg/l

Similarly, Battelle (1974), in its Gray's Harbor/Chehalis River study, included separate terms in its D.O. formulation for suspended and attached algae.

The formulations used by various investigators for benthic oxygen demand differ sufficiently to warrant special mention. Lombardo (1973) uses a constant rate expression similar to the approach of Baca and Arnett (1976). Bansal (1975) considers the overall BOD decay rate, K_1, to be composed of a decay rate fraction for suspended matter, k_1, and a decay rate fraction for benthal demands, k_3 ($K_1 = k_1 + k_3$).

Harper, as reported by Lombardo (1972), uses an expression which sets the benthal oxygen demand, D_B, constant until the dissolved oxygen concentration reaches a level where it limits exertion of the demand. At this point, the benthal oxygen demand is determined as follows:

$$D_B = \frac{KC^{0.3}}{H} \theta^{(T-20)} \qquad (2\text{-}112)$$

where K = demand coefficient

C = D.O. concentration, mg/l

H = water depth

$\theta^{(T-20)}$ = temperature correction factor

Tetra Tech (1975) and the U.S. Army Corps of Engineers (1974) consider the total benthic oxygen demand to consist of two separate components - an organic sediment oxygen demand and a benthic organism oxygen demand. In their dissolved oxygen formulation, terms for both of these oxygen sinks are included. Section 3.7 considers further the question of benthic oxygen demand.

Dissolved oxygen is very important in water quality models in the sense that it affects or controls the rate of change, and therefore the concentration, of a significant number of other system constituents. Oftentimes, in formulations for dissolved oxygen, the various source/sink components are computed elsewhere in the model and then made available for use in the oxygen balance expression. For example, the process of nitrification is generally simulated as part of the constituent mass balance for nitrogen and the necessary part of this computed information is then utilized in the oxygen computations. It follows, therefore, that when computing the dissolved oxygen sources and sinks that are incorporated in the dissolved oxygen mass balance expression, the sequence of reactions must be carefully considered.

2.5.5 Toxic Materials

The behavior of toxic compounds in an aquatic environment is quite variable and depends upon the chemical properties of the compound or substance being modeled. For simplicity, toxic compound source/sink formulations used in water quality models generally assume the following form (Baca and Arnett, 1976; Lorenzen, *et al*., 1974):

$$\frac{dT_c}{dt} = -K_t\, T_c \qquad (2\text{-}113)$$

where T_c = concentration of toxic substance, mg/l

K_t = decay rate, day^{-1}

The above expression represents a first-order decay source/sink term which is incorporated into a total mass balance expression. The total mass balance expression for toxic compounds would include, in addition to the source/sink term, advective and diffusive transport of toxic compounds and the contributions from tributary inputs.

Battelle (1974), in their model application to the Gray's Harbor/Chehalis River, included a simple nth order decay source/sink formulation to describe toxic compounds as follows:

$$\frac{dT_c}{dt} = -aT_c^{\ n} \qquad (2\text{-}114)$$

where T_c = concentration of toxic compound, mg/l

a = decay rate constant, day^{-1}

n = order of decay

Chen and Orlob (1975) and the U.S. Army Corps of Engineers (1974) use a mass balance expression to account for the "toxicity level" of an aquatic system. This toxicity level or content of the water body is then multiplied by a toxicity coefficient, β, in order to describe the mortality due to toxic effects of the various biological constituents.

The majority of the model studies reviewed did not consider specific applications where toxic compounds were simulated. In general, formulations for handling toxic compounds were included should a need arise for them in future applications. Consequently, no toxic substance coefficients or decay rate values were available.

2.5.6 Carbonate System

The carbonate system is of great importance in lakes, rivers, and estuaries. The carbon dioxide (CO_2) - bicarbonate (HCO_3^-) - carbonate ($CO_3^=$) equilibrium is the major buffer system in aquatic environments. This equilibrium directly affects the pH, which in turn can affect the biological and chemical constituents. Since algae use carbon dioxide as a carbon source during photosynthesis, this is a nutrient which can reduce the growth rate when its concentration is low.

To date, the inclusion of the carbonate system in models has been limited to formulations employing simplified kinetic expressions. Tetra Tech (1975), the U.S. Army Corps of Engineers (1974), and Chen and Orlob (1975) include a carbonate system representation which calculates the total inorganic carbon (TIC) as the sum of bicarbonate, carbonate, and carbon dioxide. Carbon dioxide is assumed to be produced by respiration and consumed by algal growth. The major source is atmospheric exchange. Harper's model, as reported by Lombardo (1973), includes a total carbon-carbon dioxide-pH system and simulates the sources and sinks accordingly.

Thomann, et al. (1975) plan to include a complete chemical model, including a representation of the kinetics of the dissolved carbon dioxide system, into their water quality models of the Great Lakes. A complete chemical representation poses a new set of problems due to the rapid rates and highly non-linear forms of the governing equations. Additional programming problems can be introduced when representing the chemical species with traditional mass balance formulations.

Thomann, et al. currently treat the carbonate equilibrium in a conventional manner. The major species considered are dissolved carbon dioxide, bicarbonate, and carbonate ion, together with the hydrogen and hydroxyl ions. Mass balance equations for each of these species are complicated by the fact that they undergo reversible ionization reactions. The individual species are extremely reactive so that a direct mass balance formulation results in equations which are nonlinear and numerically quite badly behaved.

The crux of the formulation problem, therefore, is in producing a more tractable formulation in terms of quantities which are conservative relative to these ionization reactions. The computational feasibility of including these chemical reactions in the water quality model has been explored by Thomann, et al. (1975) in a series of computations using the Rand Chemical Composition Program. It is expected that this computer program will form the basis for their chemical submodel calculation in the Great Lakes water quality models.

2.5.7 Conservative Substances

Conservative constituents may be defined as those constituents that do not undergo significant chemical decay. Substances which are commonly considered to be conservative in water quality simulations include total dissolved solids (TDS), chloride ion, alkalinity, and salinity.

Conservative substances are generally assumed to move through a water body by advection and diffusion processes alone in simulation models. Tributary inflows may also contain conservative substances which are assumed to mix with the main water body. Models typically include a mass balance expression for conservative substances with the decay rate assumed equal to zero (e.g., Tetra Tech, 1975; U.S. Army Corps of Engineers (1974), and Lam and Simons (1976)). The governing equations for conservative substances which are considered in a water quality model, therefore, are simply time-dependent advection-diffusion equations as discussed previously.

Tetra Tech (1975) uses the results from the calculation of the concentration of alkalinity, which is treated as a conservative substance, to perform a calculation for pH and carbon dioxide. Battelle (1974) treats salinity as a conservative constituent, which is advected and transported in a mass balance equation. Salinity is included in their oxygen saturation concentration calculations because it influences the rate of dissolved oxygen reaeration.

Tetra Tech (1976b), the U.S. Army Corps of Engineers (1974), and Lombardo (1973), all consider total dissolved solids as a conservative substance in their models. Total dissolved solids is generally assumed to behave as a conservative substance in models because of the difficulty of simulating all of the processes affecting total dissolved solids concentration, such as adsorption and desorption from sediments. Biological uptake of certain ions may also influence total dissolved solid concentrations, and could be a source of error when considering total dissolved solids as a conservative substance (Lombardo, 1973). Total dissolved solids concentration is of great importance because it influences the possible uses of water. The Public Health Service recommends that the total dissolved solids concentration of drinking water be less than 500 ppm and water with a concentration of total dissolved solids greater than 1,000 ppm is generally unfit for industrial purposes.

Some biological mechanisms - algal and bacterial growth for example - will decrease the concentration of certain ions; while others, such as zooplankton excretion and bacterial nutrient regeneration, will increase ion concentrations. Rainfall may also influence the total dissolved solids content of a water body when its total dissolved solids concentration is different from that of the water body. Lombardo (1973) stresses the need for verification of the conservative constituent assumption for each substance modeled as such.

In collecting field data, specific electrical conductance is used for measuring total dissolved solids concentration. The conversion relationship between conductivity and dissolved solids, however, is not perfectly linear. For most natural waters, the conversion factor ranges from 0.54 to 0.96 mg/l per micromho/cm and is usually taken as 0.65 ± 0.1 (Lombardo, 1972). Tanji and Beggar, as reported by Lombardo (1972), found the conversion factor to be 0.727 for a number of western U.S. rivers. Conductance is usually reported at 25°C. Frequently, when the dissolved solids concentration becomes high, as in seawater, the relationship between conductance and concentration is not well defined.

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CHAPTER 3

A DETAILED REVIEW OF SELECTED MODEL FORMULATIONS AND PARAMETERS

3.1 INTRODUCTION

Chapter 3 covers several aspects of water quality models not presented in Chapter 2. The approach is also different. In Chapter 2, material was organized along process lines. For example, coverage included geometric representations, mass transport, and chemical processes. Other subjects presented in Chapter 2 included such issues as numerical solution techniques and brief discussions of formulations and parameters which are either not universally simulated (e.g., "fish" and "toxic substances") or for which there are little rate data available. Chapter 3 presents several topics which are ordinarily of major importance in surface water quality modeling and which merit extended coverage. Also, discussions are arranged by water quality parameter rather than by process, as they generally were in Chapter 2.

Chapter 3 addresses the problem of selecting appropriate values for model rates and parameters. This is done by discussing the formulations and incorporated constants, factors affecting those constants, and ways of measuring the phenomena involved. Definite guidelines for the selection of rate constant values are not always available, however. Further, an effort has generally been made to avoid including material recommending a specific value under a given set of circumstances. It was felt that ordinarily, the selection of parameter values is too case-dependent, far too many factors must be considered for each situation, and presenting values to be used under set conditions would more often mislead than guide the user to a satisfactory value.

For each rate parameter discussed, mathematical expressions are presented to show how the parameter relates to the mass balance expression of which it is a part. This illustrates precisely what parameter is being discussed, and minimizes the ambiguity and possible misinterpretation of the parameter's significance and normal use. Also incorporated are values for the parameters being discussed as reported in the literature. The data presented include, in addition, various related factors which may be of use to the modeler. For example, in selecting specific growth rate values, it is important to compensate for the effect of temperature. This, in turn requires data on temperature response. In general, such temperature response data are presented in conjunction with the rate data themselves.

Finally, at the end of each section, references are presented. This was done because of the large number of sources cited and in order to facilitate the user's locating of reference material.

3.2 REAERATION

3.2.1 Introduction

The dissolution of gaseous oxygen in water can be viewed as a mass transfer process occurring in sequential steps. According to the "Two Film Theory," beginning in the vapor phase, oxygen travels through a gas film on the vapor side of the gas-liquid interface. It then passes through a liquid film on the liquid side of the interface, and is finally dispersed throughout the bulk solution.

Each of these steps requires a finite period of time. However, one particular step may take significantly longer than the other and is thus termed the rate limiting step. Under perfectly quiescent conditions the diffusion of the oxygen through the bulk liquid is the slowest step, and here, molecular diffusion expressions may be used to predict the rate of transfer of dissolved oxygen. However due to turbulance in natural systems, the bulk diffusion rate is not ordinarily rate limiting. For oxygen, or any other sparingly soluble gas, the rate limiting step becomes the passage through the liquid film. The rate limiting step for highly soluble carbon dioxide, in contrast, is passage through the gas film.

Lewis and Whitman (1924) assumed that transport through the interfacial film was affected solely by molecular action and that the process obeyed Fick's first law (Bird, et al., 1960). Assuming the concentration gradient to be linear through the film, Fick's law can be written as:

$$q = AD_m \frac{C_s - C}{\delta} \tag{3-1}$$

where q = rate of transport of oxygen through a surface, mg min^{-1}

D_m = molecular diffusivity of oxygen in water, cm^2 min^{-1}

δ = film thickness, cm

C = dissolved oxygen concentration below film, mg ml^{-1}

C_s = saturation dissolved oxygen concentration, mg ml^{-1}

A = surface area, cm^2

Letting

$$K_L = \frac{D_m}{\delta} \tag{3-2}$$

Equation (3-1) can be rewritten as

$$q = AK_L\ (C_s - C) \tag{3-3}$$

where K_L is commonly known as the oxygen transfer coefficient. Researchers have expressed K_L in terms of more readily measurable parameters, as will be shown shortly. Holley (1975) has discussed potential ramifications of the assumptions used by Lewis and Whitman in the above derivation.

Equation (3-3) can be used to determine the flux of dissolved oxygen entering (or leaving) a receiving water body through the mechanism of reaeration, and incorporates no assumptions about whether or not the water body is well-mixed. If, however, the water body is assumed to be well mixed vertically, so that a single concentration, C, exists over depth, the time rate of accumulation of dissolved oxygen due to reaeration can be expressed as:

$$V \frac{\partial C}{\partial t} = AK_L \left(C_s - C \right) \tag{3-4}$$

or

$$\frac{\partial C}{\partial t} = \left(\frac{A}{V} K_L \right) \left(C_s - C \right) \tag{3-5}$$

or

$$\frac{\partial C}{\partial t} = k_2 \left(C_s - C \right) \tag{3-6}$$

where V = volume of water under the surface area, A, cm^3

The ratio V/A equals average depth, H. The quantity K_L/H is usually expressed by a single coefficient (as shown in Equation 3-6), most commonly designated as k_a or k_2 in the literature, and commonly having units of day^{-1} or $hour^{-1}$. The notation k_2 will be used here.

3.2.2 Expressions for Reaeration Coefficient

Much research has been done to develop both empirical and mechanistically justifiable expressions for k_2 and K_L. This section will discuss a number of these expressions, and will be divided essentially into discussions of coefficients applicable to streams, to lakes, and to estuaries. Some overlap of expressions is unavoidable, however. For more exhaustive discussions on the expressions presented here (along with some others that are not) the user is referred to Covar (1976), Elmi (1975), Holley (1975), Kramer (1974), Bennett and Rathbun (1972), and Lau (1972).

Weber (1972) showed, by using dimensional analysis, that the reaeration coefficient for streams is a function of stream depth and velocity, each variable being raised to some power. Many researchers have developed expressions for k_2 that contain these variables, although other researchers have based their formulas on other variables. Table 3-1 shows a number of these expressions. In addition, the table contains information pertaining to the conditions under which the formulas were developed, the units in which the variables should be expressed, the original reference in which each formulation was reported, and more recent references discussing the expressions in detail. In Section 3.2.6 a method devised by Covar (1976) will be discussed that is useful in selecting a particular reaeration coefficient for streams.

Many rivers and streams have small to moderate sized dams crossing them in one or more places. Reaeration occurs as the water flows over the dam. Based on experimental data (Gameson, *et al.*, 1958), and later verified with field data (Barrett, *et al.*, 1960), the following relationship for reaeration over dams has been developed:

$$D_a - D_b = \left[1 - \frac{1}{1 + 0.11\,ab(1 + 0.046T)H}\right] D_a \tag{3-7}$$

where D_a = dissolved oxygen deficit above dam, mg/l

D_b = dissolved oxygen deficit below dam, mg/l

T = temperature, °C

H = height through which the water falls, ft

a = 1.25 in clear to slightly polluted water: 1.00 in polluted water

b = 1.00 for weir with free fall: 1.3 for step weirs or cascades

An alternate equation developed from data on the Mohawk River and Barge Canal in New York State (Mastropietro, 1968) is as follows:

$$D_a - D_b = 0.037HD_a \tag{3-8}$$

Equation (3-8) is valid for H up to 15 feet and for temperatures in the range of 20° to 25°C. Under these conditions, it is recommended that this equation be used in preference to Equation (3-7) because it was specifically developed for such conditions.

TABLE 3-1. REAERATION COEFFICIENTS FOR STREAMS

Original Reference	Formulation for k_2 (base e)	Units of Variables	Development Conditions	Discussed By
O'Connor and Dobbins (1958)	$\frac{(D_M \cdot U)^{0.5}}{H^{1.5}}$	Any compatible set of units	For streams displaying isotropic turbulence. The observed data had the following characteristics: $1' < H < 30'$; $0.5 < U < 1.6$ fps; $0.05 < k_a < 12.2$/day.	Covar (1976) Holley (1975)
Churchill, et al. (1962)	$\frac{11.6U^{0.969}}{H^{1.673}}$	U-fps H-feet k_2-1/day	Based on observed reaeration rates below dams from which oxygen deficient water was released. $2' < H < 11'$; $1.8 < U < 5$ fps.	Covar (1976) Holley (1975)
Owens, et al. (1964)	$\frac{21.7U^{0.67}}{H^{1.85}}$	U-fps H-feet k_2-1/day	Oxygen recovery monitored for six streams in England following deoxygenation with sodium sulfite. $0.1 < U < 5$ fps $0.4' < H < 11'$	Covar (1976)
Langbein and Durum (1967)	$\frac{7.6U}{H^{1.33}}$	U-fps H-feet k_2-1/day	Based on synthesis of data from O'Connor and Dobbins (1958), Churchill, et al. (1962), Krenkel and Orlob (1963), and Streeter, et al. (1936).	Covar (1976)
Isaacs and Gaudy (1968)	$\frac{7.03U}{H^{1.5}}$	U-fps H-feet k_2-1/day	Developed using regression analysis on data collected from a circular trough with recirculating water.	Covar (1976)
Negulescu and Rojanski (1969)	$4.74\left(\frac{U}{H}\right)^{0.85}$	U-fps H-feet k_2-1/day	Developed from a recirculating flume with depths less than 0.5 feet.	Covar (1976) Elmi (1975)
Tsivoglou (1967, 1972) Tsivoglou and Neal (1976)	$0.054\left(\frac{\Delta h}{t}\right)$ @25°C	Δh-feet t-hours k_2-1/hour	Gas tracer technique used. $25 < Q < 3000$ cfs	Covar (1976) Elmi (1975)
Foree (1976)	$0.30 + 0.19S^{1.2}$ @ 25°C	S-feet/mile k_2-1/day	Gas tracer technique used on small streams in Kentucky. $0 < S < 42$ feet/mile $.02 < q < 2.02$ cfs/sq.mile	Foree (1976)
Gloyna, et al. (1971)	$6.86\frac{U^{0.703}}{H^{1.05}}$	U-fps H-feet k_2-1/day	Regression analysis used on data for which $9.8 < k_2 < 28.8$/day	Gloyna, et al. (1971)

(continued)

TABLE 3-1 (continued)

Original Reference	Formulation for k_2 (base e)	Units of Variables	Development Conditions	Discussed By
Thackston and Krenkel (1969)	$0.000299 \left[1+\left(\frac{U_x}{\sqrt{gH}}\right)^{1/2}\right]\sqrt{\frac{Sg}{H}}$	--	--	Thackston and Krenkel (1969)
O'Connor and Dobbins (1956)	$\left(D_M \frac{U}{H}\right)^{1/2}$	--	Valid for low velocities and anisotropic conditions.	Hydrologic Engineering Center (1974)
Krenkel and Orlob (1962)	$9.9 \cdot 10^{-5}\ D_L^{\,1.150_H-1.95}$	D_L-ft^2/min k_2-1/min H-ft	Based on artificial channel observations.	Elmi (1975)

Notes:

1. All expressions given to base e and for 20°C unless otherwise noted
2. Definition of symbols:

D_M = molecular diffusion coefficient ($8.1 \cdot 10^{-5}$ ft/hr @ 20°C) for oxygen in water
U = stream velocity
H = average stream depth
Δh = change in stream elevation between two points
t = travel time between two points for which Δh measured
S = slope (change in water surface elevation divided by distance)
q = specific discharge (cfs per square mile of drainage area)
D_L = longitudinal dispersion coefficient
U_x = bed shear velocity

Foree (1976) has more recently investigated the reaeration effects of small dams in Kentucky under low flow conditions. The expression he developed is:

$$D_b = \frac{1}{r} D_a \qquad (3\text{-}9)$$

where

$$r = e^{0.16H} \quad (@\ 25°C) \qquad (3\text{-}10)$$

The value r was corrected for temperature by:

$$\ln r_{25°C} = \left(\ln r_T\right)(1.022)^{(25-T)} \qquad (3\text{-}11)$$

Foree developed this relationship within the following ranges of values:

$$2 \leq Q \leq 108 \text{ cfs}$$

$$2.6 \leq H \leq 14.0 \text{ feet}$$

$$17.0 \leq T \leq 24.0°C$$

A limited number of expressions have been developed for K_L to be used in stratified systems, such as stratified lakes or estuaries. Generally these expressions contain terms for wind velocity in addition to, or in place of, hydraulic parameters, since wind can be the major driving force inducing turbulence into the flow field. This is especially true in lake systems where the net advective velocity may approach zero. Of course K_L can be obtained from k_2 for completely mixed systems from Equation (3-6). However, for stratified systems the relationship between K_L and k_2 as expressed from Equations (3-5) and (3-6) is only valid for a depth over which the dissolved oxygen concentration can be considered constant. This depth is almost always less than the depth of the system.

Baca and Arnett (1976) have employed the surface transfer coefficient to simulate reaeration in the mixed surface layer of lakes. The expression used is:

$$K_L = a_1 + a_2 V_w \qquad (3\text{-}12)$$

where V_w = wind speed, m/day

a_1 = 0.005-0.01 day^{-1}

a_2 = 10^{-6} - 10^{-5} m^{-1}

K_L = surface transfer coefficient, day^{-1}

Kanwisher (1963) has developed an expression for the transfer coefficient that has been applied to lakes (Chen, et al., 1976). It is given by:

$$K_L = D_m / \left[\left(200-60\sqrt{V_w}\right)10^{-6}\right] \qquad (3\text{-}13)$$

where D_m = molecular diffusivity of oxygen, m^2/sec

V_w = wind speed, m/sec.

Note from Equation (3-2) that the denominator of Equation (3-13) is equivalent to δ, the liquid film thickness.

Smith (pers. comm.) has used open-sea data previously collected by Kanwisher (1963) to develop an expression (Equation (3-14)) for the transfer coefficient applicable to estuaries. This expression is given as:

$$K_L = 1.57 + 0.32\ V_w^{\ 2} \qquad (3\text{-}14)$$

where K_L and V_w are in units of feet/day and feet/second, respectively. The use of this expression is discussed by Johanson, et al. (1977).

For shallow lakes Banks (1975) developed several expressions for K_L, each applicable over a limited range of wind speeds. The relationships are:

$$K_L = 0.362\ V_w^{\ 1/2} \quad \text{for} \quad 0 \leq V_w \leq 5.5 \text{ m/sec} \qquad (3\text{-}15)$$

and

$$K_L = 0.0277\ V_w^{\ 2} \quad \text{for} \quad 5.5 \text{ m/sec} < V_w \qquad (3\text{-}16)$$

where K_L is in meters/day.

Although Banks actually developed three relationships, the third one is applicable over such a narrow range of wind speeds that the above two formulations are sufficient. By "shallow lakes" Banks implies that the vertical turbulent diffusion coefficient is constant throughout the depth of a lake.

Eloubaidy and Plate (1972) have performed experiments in the wind wave facility of Colorado State University for the purpose of determining the effect of wind on the reaeration rate in flowing water. Their ultimate objective was to develop a practical method of predicting reaeration in streams with wind blowing across the surface. They arrived at the following expression for the transfer coefficient, K_L, in feet per day:

$$K_L = \frac{C U_{*_s} h U_{*_c}}{\nu} \qquad (3\text{-}17)$$

where C = a constant of proportionality

ν = kinematic viscosity of water, m^2/sec

U_{*_s} = surface shear velocity, m/sec = $0.0185\ V_w^{1.5}$

V_w = wind, m/sec

U_{*_c} = shear velocity defined as $\sqrt{gh\ S_c}$, m/sec

h = normal depth (i.e., depth with uniform flow), m

S_c = pressure-adjusted channel slope, unitless, $S_o + \frac{1}{\rho g}\frac{dP}{dx}$

ρ = mass density of water, kg/m^3

g = gravitational constant, m/sec^2

S_o = slope of energy gradient (channel slope for uniform flow), unitless

$\frac{dP}{dx}$ = air pressure gradient in the longitudinal direction, $kg/m^2\text{-}sec^2$

From their experiments Eloubaidy and Plate found that C = .0027.

The variables comprising Equation (3-17) are readily obtainable, with the exception of the pressure gradient. For short river reaches this can be set to zero. The authors determined that an error on the order of 2% was obtained in k_2 (= K_L/h) by neglecting the pressure gradient.

A summary of the conditions under which Equation (3-17) was developed is as follows:

channel slope: .00043, .001

air velocity: 22, 30, 38 fps for each slope

discharge: 0.79, 0.83, 0.91 cfs at 0.001 slope
0.58, 10.63, 0.75 cfs at 0.0043 slope

water depth: 0.385 feet

Downing and Truesdale (1955) performed a laboratory study using a small tank and fan to generate wind currents for the purpose of comparing their results with estuary data. Their findings were not in good agreement with observed reaeration rates, and they attributed differences partly to the turbulent nature of the wind generated by the fan. Their data also indicated that below 7 mph, wind had little effect on the reaeration rate. Eloubaidy and Plate (1972), on the other hand, had found that wind began to play a significant role in reaeration at speeds above 1.6 mph. In accurately quantifying the effect of wind on reaeration Kramer (1974) hypothesized that it is not sufficient to consider wind speed alone but direction as well when dealing with inland water bodies protected by complex surrounding topographic features.

As well as using predictive relationships based on wind velocities to express reaeration in estuaries, numerous investigators have based reaeration on velocity and depth (see, for example, Johanson, et al. (1977) and Hyer, et al. (1971)). Each of these workers uses an expression developed by O'Connor (1960). O'Connor arrived at his formula from relationships developed specifically for non-tidal streams and rivers. The expression is:

$$k_2 = \frac{\left(D_m U_o\right)^{0.5}}{H^{1.5}} \tag{3-18}$$

where D_m = molecular diffusivity of oxygen

U_o = mean tidal velocity over a complete tidal cycle

H = average depth at a section over the tidal cycle

and any consistent units are used. Equation (3-18) is valid for nonstratified estuaries and was verified on the Delaware and James Rivers.

In modeling estuarine reaeration, other researchers have used expressions such as those for k_2 found in Table 3-1, which were developed for streams (Kramer, 1974). Since the reaeration expressions were not developed under estuarine flow conditions, their application to such conditions may not be justifiable.

3.2.3 Factors Affecting Reaeration

In the predictive equations presented in Section 3.2.2 it was tacitly assumed that the reaeration rate, in each case, depends only on the variables appearing in the particular expression. In most instances the variables were depth, flow velocity, and wind velocity. For streams, the flow velocity is the instantaneous velocity. For estuaries the instantaneous velocity can be used in real-time models, while for tidally averaged models, the tidally averaged velocity must be used.

Wind speed has most often appeared in expressions for the transfer coefficient for lakes and estuaries, although Eloubaidy and Plate (1972) developed an expression containing wind speed applicable to streams, as discussed earlier. A smaller number of researchers have used other variables for stream reaeration, such as channel slope (Foree, 1976) and change in water surface elevation with respect to travel time (Tsivoglou, 1967).

Other factors are also known to influence reaeration rates. These effects have been satisfactorily quantified, in some instances, while in others, they have not. The factors (from Holley, 1975) are listed below, followed by a discussion of each.

1. The Schmidt number, S_c, where $S_c = \nu/D_m$, the kinematic viscosity of the liquid divided by the molecular diffusivity of the dissolved gas. Since S_c is a function of temperature, the dependence of the reaeration coefficient on S_c can be, and often has been, replaced by an Arrhenius temperature relationship:

$$\left(k_2\right)_T = \left(k_2\right)_{20} \theta^{T-20} \quad (3\text{-}19)$$

where T = temperature at which the reaeration coefficient is to be evaluated, °C

θ = temperature adjustment factor

2. Surfactants.

3. Suspended particles.

4. Dissolved substances.

5. Artificial mixing.

In Equation (3-19), the base temperature used to evaluate reaeration is 20°C. Some researchers have preferred to use 25°C as the base temperature. The value of k_2 at 25°C can be found from Equation (3-19) to be:

$$\left(k_2\right)_{25} = \theta^5 \left(k_2\right)_{20} \quad (3\text{-}20)$$

Although k_2 has been used in both of the above two equations, K_L could as well have been used.

Table 3-2 shows values of the temperature coefficient θ for different types of systems and the reference from which each value of θ was obtained. It is important to note that the data are for a base temperature of 25°C.

TABLE 3-2. REPORTED VALUES OF TEMPERATURE COEFFICIENT
(FROM METZGER, 1968)

Temperature Coefficient, θ	Surface Transfer Coefficient, K_L, in Centimeters Per Minute	Aeration System	Reference
1.047	0.01	channel	Streeter, et al. (1936)
1.0241	0.02	stirred	Elmore and West (1961)
1.0226	-	stirred	Elmore and West (1961)
1.020	0.02	stirred	Downing and Truesdale (1955)
1.024	0.03	stirred	Downing and Truesdale (1955)
1.016	0.06	stirred	Downing and Truesdale (1955)
1.016	0.15	stream	Streeter (1926)
1.018	0.028	channel	Truesdale and Van Dyke (1958)
1.015	0.042	channel	Truesdale and Van Dyke (1958)
1.008	0.37	channel	Truesdale and Van Dyke (1958)

The range of θ's presented in Table 3-2 (1.008 to 1.047) produce reaeration rate ratios of 146 percent and 68 percent at 30° and 10°C, respectively, when a base temperature of 20°C is used. The ramifications of this are that by using an incorrect θ for a particular system, the dissolved oxygen resource estimates for the system can be quite inaccurate.

Metzger (1968) undertook a study to determine the reasons behind the variation in θ values reported from the literature. He found that for higher mixing (more turbulence) the surface transfer coefficient increased. This, in turn, decreased θ. Figure 3-1 shows the results of Metzger's work, along with the θ values shown earlier in Table 3-2. Metzger's formula for K_L, using film penetration theory, will not be presented here. However, Metzger found that for low mixing intensity (surface water smooth), K_L ranged from 0.10 to 0.12 cm/min at 20°C, and for moderate mixing intensity (water surface mildly rippled) K_L was approximately 0.40 cm/min.

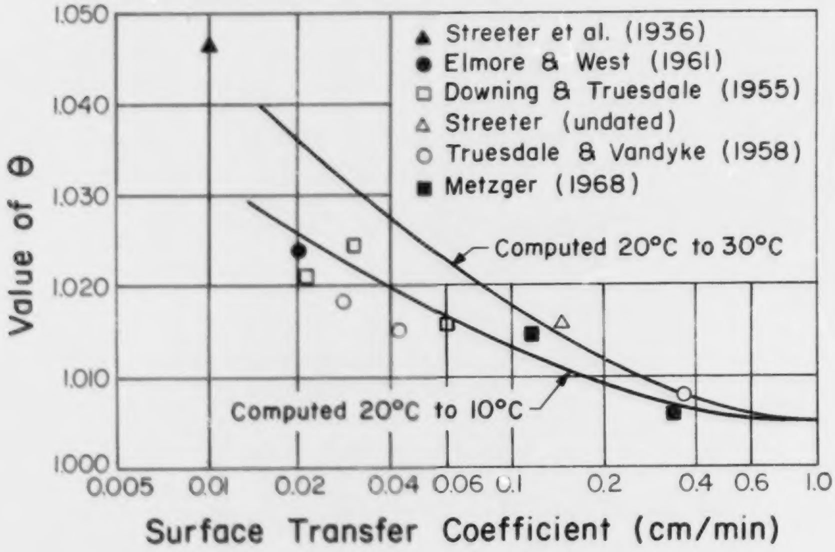

Figure 3-1. Effects of the surface transfer coefficient (K_L) on the value of θ in Equation (3-19) (Metzger, 1968).

Surface active agents (SAA) tend to decrease atmospheric reaeration by reducing the surface transfer coefficient, K_L (Mancy and Barlage, undated). The extent of reduction depends upon the hydrodynamic characteristics of the liquid phase and the physicochemical characteristics of the SAA. Resistance to oxygen transfer has been shown to result from two kinds of effects:

1. physical interference of SAA molecules, and
2. increase in viscosity of the interfacial liquid.

Conflicting results have been obtained in the few studies which examine the effects of suspended solids on reaeration rates (Holley, 1975). These conflicting results prompted Alonso, et al. (1975) to perform a study of the effect of suspended sediment loads on reaeration rates in sediment-laden flows in straight open channels. Alonso, et al. compared the results with the surface reaeration rates observed in clear water open channel flows having the same bulk-flow characteristics. From their experiments they concluded that the reaeration rate decreased about 35% over the sediment concentration range used (up to 3,562 ppm). This decrease in k_2 was attributed to the decrease in the intensity of turbulent mixing at higher suspended sediment loads, which, in turn, decreases reaeration.

Poon and Campbell (1967) investigated the effects of dissolved chemicals on the rate of oxygen transfer using water column aeration by submerged diffusers. They found that by increasing the concentrations and molecular weights of dissolved chemicals, the rate of oxygen transfer due to the rising bubbles was reduced. The results of Poon and Campbell are summarized in Table 3-3, where α is defined as the ratio of the diffusion coefficients with to without the dissolved substances.

TABLE 3-3. SURFACE TRANSFER RATIO α
FOR VARIOUS SUBSTANCES (FROM POON AND CAMPBELL, 1967)

Dissolved Matter	Concentration mg/l	Ratio α
Sodium Chloride	1000	0.99
Glycine	1000	0.92
Glucose	1000	0.90
Soluble Starch	1000	0.87
Peptone	1000	0.51
Nutrient Broth	1000	0.47

Artificial reaeration by means of mechanical aerators will not be discussed here (see, for example, Whipple, *et al*. (1969), and Weber (1972). However, it should be noted that reaeration due to ship mixing may be of importance in certain situations. In the Houston Ship Channel, Kramer (1974) attempted to predict reaeration based on several predictive formulas, such as are shown in Table 3-1. In all cases the predicted values were considerably less than observed. The author felt that this discrepancy was due largely to artificial mixing induced by ship traffic and wind effects.

3.2.4 Tabulated Values of the Reaeration Coefficient

Tables 3-4 and 3-5 below show reaeration coefficients and other characteristics of streams and rivers as taken from Hydroscience (1971) and Elmi (1975). Table 3-6 shows reaeration coefficients observed in tidal rivers and estuaries. Included in the tables are data on hydraulic characteristics of the systems, as well as original references. Additional values for stream reaeration rates are included in Table 3-17 in Section 3.6 on "Nitrogenous Deoxygenation." Some duplication exists between that table and Tables 3-4 and 3-5.

Because they are based upon hydraulic type variables which are readily quantifiable, reaeration rates for streams, rivers, and estuaries have been extensively computed and tabulated (see, e.g., Table 3-1). Since these values generally do not change substantially over time, the values in the tables may give reasonable estimates of the reaeration rate for the systems tabulated. For lakes, however, reaeration has generally been expressed as a function of wind speed, and is not closely related to lake characteristics. Hence there are no "typical" values of K_L or k_2 for a particular lake, and no tabulations will be given here. Referral to Section 3.2.2, however, will show expressions based on wind speed for K_L.

3.2.5 Techniques Used to Estimate Reaeration in Situ

Many methods have historically been used to estimate the reaeration rate in receiving water bodies. One approach consists of using a mass-balance equation for dissolved oxygen where all the parameters except k_2 are measured, leaving k_2 to be calculated. Churchill, *et al*. (1962) have used this approach and expressed k_2 in terms of the dissolved oxygen deficit observed at two points in a stream:

$$k_2 = \frac{\ln D_o - \ln D_1}{t} \qquad (3\text{-}21)$$

where D_o = deficit at upstream location, mg/l

D_1 = deficit at downstream location, mg/l

t = time of travel between the two locations, days

TABLE 3-4. REAERATION COEFFICIENTS AND OTHER CHARACTERISTICS OF STREAMS AND RIVERS (AFTER HYDROSCIENCE, 1971)

River Name	Category	Depth (ft.)	Area (ft^2)	Flow (cfs)	Velocity (fps)	K_L (ft/day)	k_2 @20°C (1/day)	k_d* @20°C (1/day)	Reference
Grand River (Michigan)	Shallow	1.9	320.0	295.	0.92		4.5	0.59	O'Connor and Di Toro (1970)
Clinton R. (Michigan)	Shallow	1.58	44.6	33.	0.72		5.9	3.37	O'Connor and Di Toro (1970)
Truckee R. (Nevada)	Shallow	1.67	150.	180.	1.20		5.6	0.36	O'Connor and Di Toro (1970)
		1.67	150.	195.	1.30		5.7	0.36	
		1.67	150.	271.	1.81		6.6	0.96	
Flint River (Michigan)	Shallow	2.1	210.	134.	0.64		3.5	0.56	O'Connor and Di Toro (1970)
		2.6	200.	174.	0.83		3.9	0.63	
		2.6	400.	174.	0.44		3.1	0.69	
		1.7	290.	204.	0.73		5.0	0.69	
		1.9	400.	204.	0.51		2.2	0.69	
Jackson R. (Virginia)	Shallow	3.	365.	100.	0.27		4.1	1.25	O'Connor with Hydroscience (1962a), (1962b), Hydroscience (1967b)
N. Branch Potomac R. (Md., W.Va.)	Shallow	2.	100.	100.	1.0		9.0	0.40	Hydroscience (1969a)
Clarion R. (Penna.)	Shallow	1.		1-10.				3.	O'Connor and Dobbins (1958)
		1.9			0.55	9.	2.26		
South River		1-2		35.				2.	
Ivel River (England)	Shallow	1.21		4.86	0.14	5.58	2.35		Owens, et al. (1964)
		1.51		4.15	0.14	4.64	2.06		
		1.09		3.87	0.13	6.83	3.20		
		1.50		15.40	0.37	6.45	2.37		
		1.08		4.86	0.16	9.75	4.57		
		0.38		4.15	0.15	4.00	2.09		
		1.12		3.87	0.13	2.55	1.18		
		1.46		15.40	0.38	8.65	3.18		
		1.31		15.40	0.47	14.70	6.18		
		2.44		10.07	0.23	4.16	0.90		
		2.03		10.07	0.22	6.35	1.66		

*k_d is the deoxygenation coefficient. See Section 3.5.

(continued)

TABLE 3-4 (continued)

River Name	Category	Depth (ft.)	Area (ft^2)	Flow (cfs)	Velocity (fps)	K_L (ft/day)	k_2 @20°C (1/day)	k_d* @20°C (1/day)	Reference
Lark River (England)	Shallow	1.74		10.94	0.28	2.48	0.78		
		1.47		10.94	0.37	6.04	2.12		
		1.82		36.20	0.50	5.10	1.41		
		2.41		36.20	0.43	1.48	0.31		
Derwent R. (England)	Shallow	0.72		21.60	1.37	41.90	31.80		Owens, et al. (1964)
		0.89		21.60	1.19	39.70	24.53		
		0.85		21.60	1.07	37.80	34.57		
Black Beck River (England)	Shallow	0.40		2.70	0.44	19.30	25.59		Owens, et al. (1964)
		0.40		2.70	0.56	20.90	28.34		
		0.39		2.70	0.63	21.00	22.80		
		0.60		17.70	1.83	54.80	49.17		
		0.69		17.70	1.81	39.40	30.77		
		1.00		17.70	1.54	34.20	18.46		
St. Sunday's Beck (Eng.)	Shallow	0.82		19.10	1.07	32.40	21.05		Owens, et al. (1964)
		0.78		19.10	1.27	23.70	16.06		
Yewdale Beck (England)	Shallow	0.64		5.10	0.46	14.40	12.04		Owens, et al. (1964)
		0.48		5.10	0.60	19.20	30.32		
		0.72		17.30	1.16	25.30	18.90		
		0.66		17.30	1.31	24.80	20.25		
		0.67		17.30	1.30	21.10	17.09		
		0.69		17.30	1.25	24.60	19.16		
Elk River (Penna.)	Shallow	0.9			0.97	12.	5.84		O'Connor and Dobbins (1958)
Mohawk River	Shallow	3.	143.				.07-4.0	.23	O'Connor & Hydroscience (1967)
Mohawk River (New York)	Intermediate	15.	3800.	800.	.21		.07-4.0	.40	O'Connor & Hydroscience (1968)
North Branch Susquehanna	Intermediate	4.	1700.	1000.	0.60		1.5	0.35	Hydroscience (1965a)
New River (Virginia)	Intermediate	5.	1720.	1200.	0.70		1.04	2.5 0.5	Hydroscience,(1966a) Hydroscience,(1967a)

*k_d is the deoxygenation coefficient. See Section 3.5.

(continued)

TABLE 3-4 (continued)

River Name	Category	Depth (ft.)	Area (ft^2)	Flow (cfs)	Velocity (fps)	K_L (ft/day)	k_2 @20°C (1/day)	k_d^* @20°C (1/day)	Reference
Wabash (Indiana)	Intermediate	5-7		1000-5000				.40	
Clinch R. (T.V.)	Intermediate	3.27		3300	3.07	17.1	2.27		Churchill, et al. (1962)
		5.09		4500	3.69	16.2	1.44		
		4.42		3190	3.10	10.0	.98		
		6.14		5090	2.68	7.0	.50		
		5.65		5910	2.78	9.5	.74		
		7.17		5930	2.64	18.7	1.13		
Holston (T.V.)	Intermediate	11.41		10,385	2.92	7.4	.28		Churchill, et al. (1962)
		2.12		3230	2.47	16.4	3.36		
		2.93		6400	3.44	18.9	2.79		
		4.54		14,085	4.65	16.3	1.57		
		9.50		10,440	3.94	9.7	.46		
		6.29		6540	2.51	5.6	.39		
		7.52		10,500	3.15	4.7	.27		
		7.07		10,500	3.30	3.0	.55		
		5.44		5590	3.11	6.8	.54		
		8.06		11,930	4.28	11.2	.60		
		3.98		952	2.73	11.2	1.25		
Fr. Broad (T.V.)	Intermediate	9.38		12,010	2.41	5.9	.27		Churchill, et al. (1962)
		10.19		17,120	3.06	5.3	.23		
		3.29		44,105	2.40	14.2	1.88		
		4.74		8775	3.46	9.2	.84		
		5.72		12,455	4.02	8.1	.88		
		6.98		17,270	52.	14.7	.91		
		4.29		4150	85.	9.3	1.00		
		6.01		8775	.75	1.6	.55		
		7.16		12,455	.23	14.5	.98		
		9.49		17,270	3.71	4.9	.25		
Wautaga R. (T.V.)	Intermediate	3.42		3112	5.0	43.8	5.6		Churchill, et al. (1962)
Hiwassee R. (T.V.)	Intermediate	3.02		1145	3.05	11.9	1.7		Churchill, et al. (1962)
		2.83		1145	3.91	21.0	3.2		

$^*k_d$ is the deoxygenation coefficient. See Section 3.5.

(continued)

TABLE 3-4 (continued)

River Name	Category	Depth (ft.)	Area (ft^2)	Flow (cfs)	Velocity (fps)	K_L (ft/day)	k_2 @20°C (1/day)	k_d* @20°C (1/day)	Reference
Ohio River	Deep	32.	43,000	6000	.14		.06	0.25	Streeter and Phelps (1925) Hydroscience (1968b) Malcolm Pirnie (1969)
Upper Hudson (Troy, N.Y.-Saugerties)	Deep	17.5	6000	3000	0.5		.34	.125	Hydroscience (1965a)
		21.0	6750	4500	1.5		.34	.165	
Lower Sacramento R.	Deep	15-20	8000	10,000	1.5		.28	.40	Hydroscience (1964e)
							.15		
							.24		
Upper James River (Va.)	Deep	13.5	11,500	1800	0.16		.15	.48	O'Connor (1963b)
			14,500	2600	0.18		.14	.30	Hydroscience (1964d)
			14,500	9000	0.63		.12	.31	
			14,000	7500	0.53		.13	.41	
			14,500	4500	0.31		.22	.39	
			13,500	3800	0.28		.24	.38	
			15,000	1350	0.13		.22	.43	
Illinois R.	Deep	10-12		8000				.07	O'Connor and Dobbins (1958)
		9.2			1.37	6.	.225		
		9.0			1.57	7.	.269		
		8.9			1.63	7.	.224		

*k_d is the deoxygenation coefficient. See Section 3.5.

TABLE 3-5. HYDRAULIC CHARACTERISTICS AND REAERATION RATES OBSERVED BY TSIVOGLOU-WALLACE FOR FIVE RIVERS (FROM ELMI, 1975)

River	Length Studied	Flow (cfs)	Velocity (ft/sec)	Depth (ft)	Elevation Change (ft)	k_2 Observed by Gas Tracer
Flint	9.9 mi.	5-27	.31-.88	.82-1.96	8.1-57.8	.101-.698/hr @ 25°C
South	18.3 mi.	47-207	.82-1.27	1.05-2.4	2.1-47.7	.125-.324/hr @ 25°C
Chatahoochee	120.0 mi.	1070-3300	1.72-2.45	3.62-7.66	1.2-17.8	.029-.061/hr @ 25°C
Patuxent	7.0 mi.	9.8-19.5	.22-.39	.8-1.1	4.8-29.6	.101-.199/hr @ 25°C
Jackson	--	90-130	.321-.673	1.67-3.14	9.2-47.16	.07 -.364/hr @ 25°C

TABLE 3-6. REAERATION COEFFICIENTS AND OTHER CHARACTERISTICS OF TIDAL RIVERS AND ESTUARIES (AFTER HYDROSCIENCE, 1971)

Name	Depth (ft.)	Area (ft^2)	Net Non-Tidal Flow (cfs)	Advective Velocity (fps)	Dispersion Coef. $\left(\frac{mi^2}{day}\right)$	k_d @20°C $\left(\frac{1}{day}\right)$	k_2 @20°C $\left(\frac{1}{day}\right)$	Reference
Delaware R. Estuary	25.	20,000 75,000 150,000 270,000	2,500	.12 .033 .016 .009	5.	0.3	0.17	Hydroscience (1966c) Hydroscience (1969b) O'Connor (1963a)
Hudson River	35.	135,000	5,000	0.037	20.	0.25	0.09	Hydroscience (1964a,1964b,1964c,1968a)
East River	40.	80,000	0	0.	10.	0.23	0.08	Eckenfelder and Hydroscience (1968) Hydroscience (1970b)
Cooper River (S. Carolina)	40.	40,000	10,000	0.25	30. ↓ 50.	0.30	0.08	Hydroscience (1965b)
Savannah River (Ga., S.C.)	10. ↓ 28.	10,000 ↓ 40,000	7,000	0.7 0.17	10. ↓ 20.	0.30	0.1 ↓ 0.65	Hydroscience (1970c)
Lower Raritan River (N.J.)	14. 17.5	3,200 5,000	150	.047 .029	5.	0.20	0.32 0.18	Hydroscience (1964a, 1965c)
South River (N.J)	12.	2,500	23	0.01	5.	0.20	0.40	Hydroscience (1964a)
Houston Ship Channel (Tex)	25.	17,500 25,000	900 2,600	.05 .10	27. 40.	0.25	0.10	Hydroscience (1970d)
Cape Fear R. Estuary (N.C.)	9.7 20. 13.0	2,100 9,700 33,000	1,000	.48 .10 .03	2. 10.	0.23	0.3 0.1 0.37	Hydroscience (1966b)

(continued)

TABLE 3-6 (continued)

Name	Depth (ft.)	Area (ft^2)	Net Non-Tidal Flow (cfs)	Advective Velocity (fps)	Dispersion Coef. $\left(\frac{mi^2}{day}\right)$	k_d @20°C $\left(\frac{1}{day}\right)$	k_2 @20°C $\left(\frac{1}{day}\right)$	Reference
Potomac River	10. ↓ 25.	100,000 ↓ 1,700,000	550	.006 .0003	1.0 ↓ 10.	0.47	0.38	Hydroscience (1970a)
Compton Creek (New Jersey)	14.5 10.5	1,000 790	10	.010 .013	1.0	0.23	0.3 0.48	Hydroscience (1964b)
Wappinger & Fishkill Cks. (New York)	9. 4.	500 2,000	2	.004 .001	0.5 1.0	0.30	0.25	
River Foyle Estuary (N. Ireland)	10. 15. 25. 5.	10,000 15,000 20,000 40,000	250	.025 .017 .013 .006	5. 5. 5. 5.	0.30	0.29 0.22 0.10 1.16	

In order for Equation (3-21) to be valid, all processes affecting the dissolved oxygen level other than atmospheric reaeration (such as dilution, dispersion, deoxygenation processes, and photosynthesis), must be negligible. In the Churchill, et al. study the average BOD_5 in the stream reach under consideration was only 0.8 mg/l, and they deemed the deoxygenation process to be negligible.

A consideration of importance equal to the assumptions discussed above for Equation (3-21) is an accurate determination of the saturation value of dissolved oxygen, which is needed to compute the deficits D_0 and D_1. Isaacs and Gaudy (1968) have shown that errors from 5 to 50 percent can occur in the prediction of k_2 due to poor determination of the deficits.

Additional methods can be developed to determine k_2 based on other versions of the dissolved oxygen mass balance equation. When this is done, care should be taken to assure that the assumptions underlying the particular mass balance expression are met for the system to which it is being applied. An equally important consideration is that increasing complexity of the mass balance equation means more parameter estimates, and potentially, a larger error can be incorporated into the estimation of k_2.

Hornberger and Kelly (1975) have adapted the work of Odum (1956) in developing two productivity-based methods for prediction of reaeration in streams. The first method uses observed nighttime changes in oxygen concentration, and the second compares daytime net productivity with incident radiation. These methods require that several assumptions be made:

1. productivity is linearly related to incident light,
2. nighttime respiration is constant, and
3. the reaeration coefficient is constant over a single day (this implies steady-state flow and constant water temperature).

The authors suggest that one advantage of these methods over many others is their amenability for use with automatic recording equipment. Odum's method (unmodified) has been applied successfully to estuaries (Juliano, 1969).

A radioactive tracer technique originally developed and applied by Tsivoglou (1967, 1972), Tsivoglou, et al. (1965, 1968), and Tsivoglou and Wallace (1972), and later applied by Foree (1976) has been found useful for predicting reaeration in small streams. This method does not require measurement of dissolved oxygen saturation, as many other methods do. The application of the tracer technique involves the use of tritiated water, dissolved krypton-85, and a fluorescent dye (Foree, 1976). The tracer study provides for evaluation of gas exchange capacity, time of flow, and longitudinal and total dispersion.

The reaeration coefficient is calculated from:

$$k_2 = \frac{\ln \frac{R_u}{R_d}}{0.83\ t_f} \qquad (3\text{-}22)$$

where R_u, R_d = measured ratios of krypton-85 activity to tritium activity at the upstream and downstream ends of the reach, respectively

t_f = time of passage of the dye peak through the reach, in days

0.83 = ratio of exchange coefficient for krypton to exchange coefficient for oxygen

The sulfite technique (Owens, et al., 1964) is also applicable to reaeration measurement in flowing waters. The water is first deoxygenated, and the rate of oxygenation is observed. For lakes or estuaries the dome method has been developed (Copeland and Duffer, 1964). Juliano (1969) later applied this technique to a location in the Sacramento-San Joaquin Estuary, California.

3.2.6 Evaluating Reaeration for a Particular System

In contrast to some other parameters, such as the deoxygenation rate, where choosing a value for the parameter is the basic issue of concern, the issue involved here is choosing an appropriate formulation for the system to be simulated. The traditional approach chosen by most modelers has been to neglect the contribution of wind to the reaeration rate in streams and to use a formulation based only on hydraulic parameters. However, for many estuary and lake simulations, especially where net advective flow is small, wind effects should be included.

Certainly there is no lack of expressions available from which to predict reaeration. However, there has been a lack of generalized approaches with which to select appropriate expressions in a given situation. One exception to this is the work done by Covar (1976) that is applicable to streams. He plotted the data used by three groups of researchers (O'Connor and Dobbins (1958), Churchill, et al. (1962), and Owens, et al. (1964)) for the reaeration expressions they developed (see Figure 3-2). These expressions were based on stream velocity and depth. The "A" line which divides the data of O'Connor and Dobbins from that of Churchill, et al. is also the line where the two equations formulated by these authors yield identical results. That this line separates the two data sets so discretely lends credence to the work of both groups. Covar arbitrarily set the "B" line at a depth of two feet to define the region containing most of the data of Owens, et al. For each of the three areas Covar calculated the reaeration equation, and plotted families of curves (Figure 3-3).

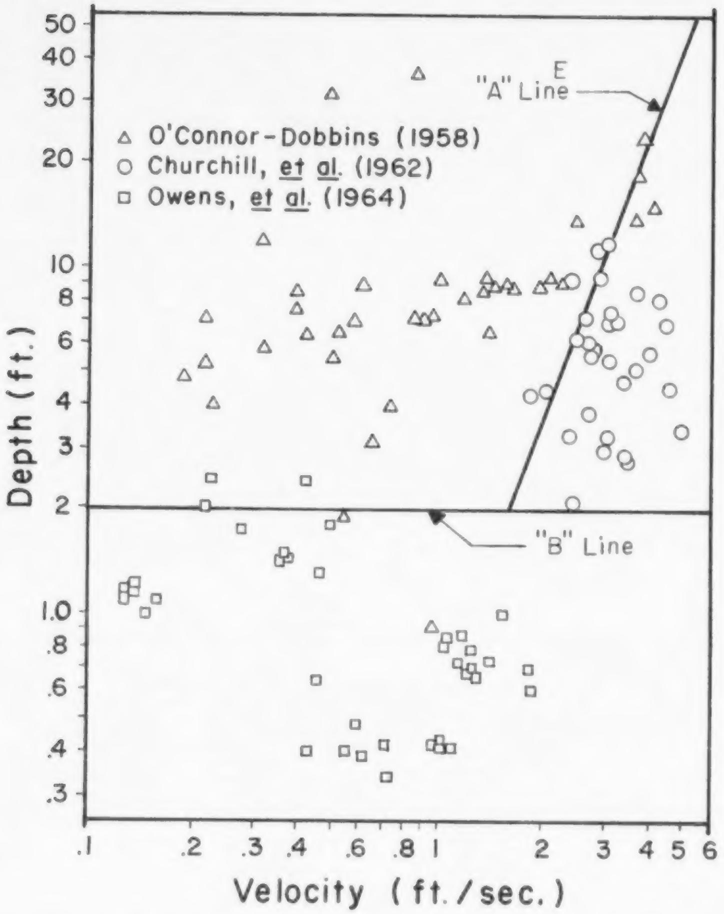

Figure 3-2. Field data considered by three different investigators (Covar, 1976).

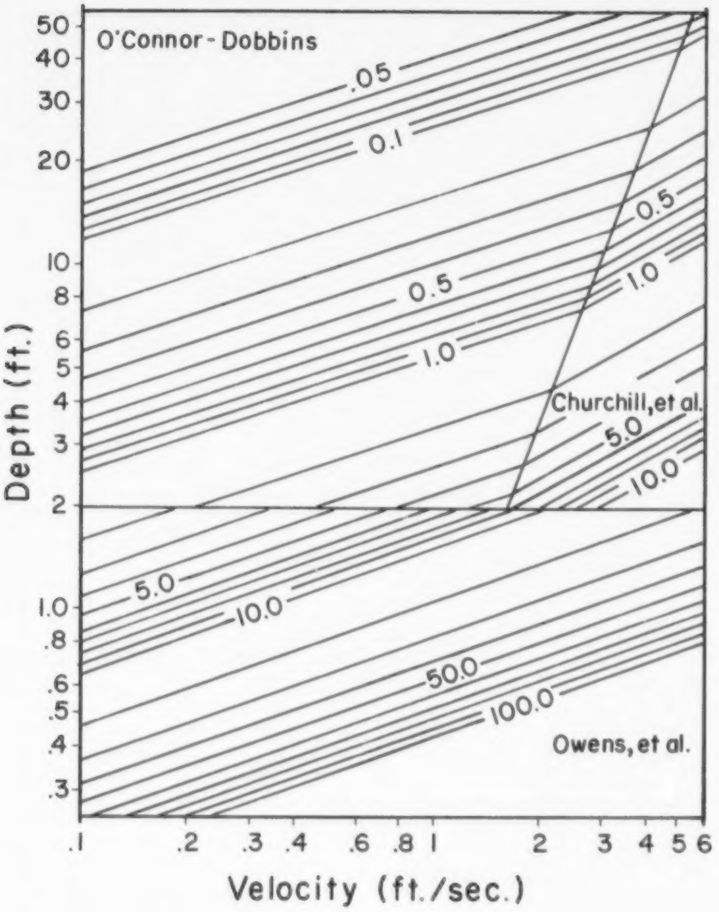

Figure 3-3. k_2 vs. depth and velocity using the suggested method of Covar (1976).

While the match-up of reaeration values along the "B" line is not exact, along the "A" line it is. Thus, Covar has developed a method of predicting stream aeration as a function of velocity and depth for streams with velocities of up to six feet per second and depths of up to 50 feet.

For non-stratified estuaries, and especially tidally influenced rivers, O'Connor's (1960) formulation has probably been the most widely applied expression containing the variables velocity and depth. This expression, however, does not account for reaeration due to wind.

Since the temperature correction factor, as previously discussed, can result in significant variations in the prediction of k_2, some consideration should be given to its choice. The guidelines of Metzger (1968) can be used to make this estimate. If K_L (as needed in Metzger's method) cannot be estimated, then it may be expedient to use a θ in the "middle range" (i.e., 1.01 to 1.025) rather than at either extreme. More accurate determinations of θ can be obtained by making measurements of k_2 at different temperatures and plotting the logarithm (base 10) of k_2 versus temperature. The slope of the resulting line is the logarithm of θ, or

$$\theta = \exp\ (2.3\ \text{slope}) \tag{3-23}$$

where the "slope" line should be the line of best fit through the plotted points.

Since each predictive formula has a limited number of variables, the user should consider whether any other effects could be important for the system being modeled. In particular, wind effects (for formulas depending only on hydraulic variables), suspended solids, and surfactants may be extraneous variables whose effect on reaeration is not quantifiable (to date) but which are, nevertheless, important determinants of reaeration.

3.2.7 References

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3.3 DISSOLVED OXYGEN SATURATION

3.3.1 *Introduction*

Dissolved oxygen saturation, commonly symbolized as C_s and expressed in mg/l, is a basic parameter used in a great many surface water quality models. Since dissolved oxygen prediction is often the reason for developing a water quality model, accurate values of C_s are needed. Additionally, values of dissolved oxygen saturation are often used in the estimation of other parameters, such as the reaeration coefficient as discussed previously in Section 3.2.5.

Use of inaccurate C_s values can lead to poor values of other parameters. Isaacs and Gaudy (1968) showed, for example, that predicted k_2 values could be in error by as much as 50 percent based on incorrect estimates of C_s.

3.3.2 *Factors Affecting Dissolved Oxygen Solubility*

The solubility of dissolved oxygen in water decreases with increasing temperature, increasing chloride concentration (or concentration of ionic impurities in general), and decreasing atmospheric pressure (i.e., partial pressure of oxygen in the atmosphere). Each of these factors has been quantified (although not always with consistent results) and will be discussed here.

The APHA (1971) presents a tabulation of oxygen solubility in water as a function of both chloride concentration (chlorinity) and water temperature (see Table 3-7). These calculations were made by Whipple and Whipple (1911), for conditions in which the water was in contact with dry air containing 20.90 percent oxygen. Since chlorinity is related to salinity, and salinity is more often measured than chlorinity, the relationship between the two quantities is of interest. The relationship is:

$$\text{Salinity (ppt or ‰)} = 0.03 + 0.001805 \text{ Chlorinity (mg/l)} \qquad (3\text{-}24)$$

In 1960, Elmore and Hayes prepared a report for the American Society of Civil Engineers concluding that the values in APHA (1971) tend to be high within a temperature range of 10°C to 30°C while being substantially correct in the temperature range 0°C to 5°C (Table 3-8). The authors concluded that since their own results were corroborated by several other workers in the field (e.g., Winkler (1891) and Morris (1959)), the values listed in Table 3-8 are more satisfactory for application to natural stream conditions. Unfortunately there is no concensus among researchers on which set of data is the better. Holley, et al. (1970), for example, found dissolved oxygen saturation values to differ from those in Table 3-8, by a substantial amount in some cases (1-1.5 mg/l).

Elmore and Hayes (1960) developed a predictive formula for C_s from the data in Table 3-8:

$$C_s = 14.652 - 0.41022T + 0.0079910T^2 - 0.000077774T^3 \qquad (3\text{-}25)$$

where C_s = dissolved oxygen saturation, mg/l

T = water temperature, °C

Equation (3-25) is valid at standard pressure and zero salinity.

Several investigators have quantified the solubility of dissolved oxygen as a function of salt content, as well as temperature. Fair, et al. (1968) found that oxygen solubility in saline waters could be approximated by multiplying the solubility in freshwater by a reduction factor. The following relationship results:

$$C_s = C_{so} \left[1 - \left(\bar{s} \times 10^{-5}\right)\right] \qquad (3\text{-}26)$$

where C_{so} = solubility at zero salinity, mg/l

$\bar{s}$ = salinity of water expressed as chloride, mg/l

If values of C_{so} are used from APHA (1971) as shown in Table 3-7, Equation (3-26) predicts the remainder of the values in that table within 0.1 mg/l,

TABLE 3-7. SOLUBILITY OF OXYGEN IN WATER
(APHA, 1971)

Temp. in °C	Chloride Concentration in Water - mg/l					Difference per 100 mg Chloride
	0	5,000	10,000	15,000	20,000	
	Dissolved Oxygen - mg/l					
0	14.6	13.8	13.0	12.1	11.3	0.017
1	14.2	13.4	12.6	11.8	11.0	0.016
2	13.8	13.1	12.3	11.5	10.8	0.015
3	13.5	12.7	12.0	11.2	10.5	0.015
4	13.1	12.4	11.7	11.0	10.3	0.014
5	12.8	12.1	11.4	10.7	10.0	0.014
6	12.5	11.8	11.1	10.5	9.8	0.014
7	12.2	11.5	10.9	10.2	9.6	0.013
8	11.9	11.2	10.6	10.0	9.4	0.013
9	11.6	11.0	10.4	9.8	9.2	0.012
10	11.3	10.7	10.1	9.6	9.0	0.012
11	11.1	10.5	9.9	9.4	8.8	0.011
12	10.8	10.3	9.7	9.2	8.6	0.011
13	10.6	10.1	9.5	9.0	8.5	0.011
14	10.4	9.9	9.3	8.8	8.3	0.010
15	10.2	9.7	9.1	8.6	8.1	0.010
16	10.0	9.5	9.0	8.5	8.0	0.010
17	9.7	9.3	8.8	8.3	7.8	0.010
18	9.5	9.1	8.6	8.2	7.7	0.009
19	9.4	8.9	8.5	8.0	7.6	0.009
20	9.2	8.7	8.3	7.9	7.4	0.009
21	9.0	8.6	8.1	7.7	7.3	0.009
22	8.8	8.4	8.0	7.6	7.1	0.008
23	8.7	8.3	7.9	7.4	7.0	0.008
24	8.5	8.1	7.7	7.3	6.9	0.008
25	8.4	8.0	7.6	7.2	6.7	0.008
26	8.2	7.8	7.4	7.0	6.6	0.008
27	8.1	7.7	7.3	6.9	6.5	0.008
28	7.9	7.5	7.1	6.8	6.4	0.008
29	7.8	7.4	7.0	6.6	6.3	0.008
30	7.6	7.3	6.9	6.5	6.1	0.008
31	7.5					
32	7.4					
33	7.3					
34	7.2					
35	7.1					

TABLE 3-8. DISSOLVED OXYGEN SATURATION VALUES IN DISTILLED WATER (ELMORE AND HAYES, 1960)

Temperature	Dissolved Oxygen in Milligrams Per Liter									
°C	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	14.65	14.61	14.57	14.53	14.49	14.45	14.41	14.37	14.33	14.29
1	14.25	14.21	14.17	14.13	14.09	14.05	14.02	13.98	13.94	13.90
2	13.86	13.82	13.79	13.75	13.71	13.68	13.64	13.60	13.56	13.53
3	13.49	13.46	13.42	13.38	13.35	13.31	13.28	13.24	13.20	13.17
4	13.13	13.10	13.06	13.03	13.00	12.96	12.93	12.89	12.86	12.82
5	12.79	12.76	12.72	12.69	12.66	12.62	12.59	12.56	12.53	12.49
6	12.46	12.43	12.40	12.36	12.33	12.30	12.27	12.24	12.21	12.18
7	12.14	12.11	12.08	12.05	12.02	11.99	11.96	11.93	11.90	11.87
8	11.84	11.81	11.78	11.75	11.72	11.70	11.67	11.64	11.61	11.58
9	11.55	11.52	11.49	11.47	11.44	11.41	11.38	11.35	11.33	11.30
10	11.27	11.24	11.22	11.19	11.16	11.14	11.11	11.08	11.06	11.03
11	11.00	10.98	10.95	11.93	10.90	10.87	10.85	10.82	10.80	10.77
12	10.75	10.72	10.70	10.67	10.65	10.62	10.60	10.57	10.55	10.52
13	10.50	10.48	10.45	10.43	10.40	10.38	10.36	10.33	10.31	10.28
14	10.26	10.24	10.22	10.19	10.17	10.15	10.12	10.10	10.08	10.06
15	10.03	10.01	9.99	9.97	9.95	9.92	9.90	9.88	9.86	9.84
16	9.82	9.79	9.77	9.75	9.73	9.71	9.69	9.67	9.65	9.63
17	9.61	9.58	9.56	9.54	9.52	9.50	9.48	9.46	9.44	9.42
18	9.40	9.38	9.36	9.34	9.32	9.30	9.29	9.27	9.25	9.23
19	9.21	9.19	9.17	9.15	9.13	9.12	9.10	9.08	9.06	9.04
20	9.02	9.00	8.98	8.97	8.95	8.93	8.91	8.90	8.88	8.86
21	8.84	8.82	8.81	8.79	8.77	8.75	8.74	8.72	8.70	8.68
22	8.67	8.65	8.63	8.62	8.60	8.58	8.56	8.55	8.53	9.52
23	8.50	8.48	8.46	8.45	8.43	8.42	8.40	8.38	8.37	8.35
24	8.33	8.32	8.30	8.29	8.27	8.25	8.24	8.22	8.21	8.19
25	8.18	8.16	8.14	8.13	8.11	8.10	8.08	8.07	8.05	8.04
26	8.02	8.01	7.99	7.98	7.96	7.95	7.93	7.92	7.90	7.89
27	7.87	7.86	7.84	7.83	7.81	7.80	7.78	7.77	7.75	7.74
28	7.72	7.71	7.69	7.68	7.66	7.65	7.64	7.62	7.61	7.59
29	7.58	7.56	7.55	7.54	7.52	7.51	7.49	7.48	7.47	7.45
30	7.44	7.42	7.41	7.40	7.38	7.37	7.35	7.34	7.32	7.31

except for within the temperature range of 0°C to 5°C at a chloride concentration of 15,000 to 20,000 mg/l. Within this region, discrepancies of up to 0.4 mg/l occur.

From the data of Green and Carritt (1967), Hyer, et al. (1971) developed an expression relating C_S to both temperature and salinity. C_S is given by:

$$\begin{aligned} C_s &= 14.6244 - 0.367134T + 0.0044972T^2 \\ &\quad - 0.0966S + 0.00205ST + 0.0002739S^2 \end{aligned} \tag{3-27}$$

where T = temperature, °C

S = salinity, ppt.

At zero salinity, the values predicted for C_S by Equation (3-27) agree with the values in Table 3-7 to within 0.1 mg/l, and with the values in Table 3-8 to within 0.2 mg/l. For nonzero salinity, Equation (3-27) agrees with the values in Table 3-7 to within 0.1 to 0.2 mg/l except for temperatures between 21 to 30°C with a chloride concentration of 15,000 to 20,000 mg/l. In this region a departure of from 0.2 to 0.7 mg/l occurs.

Barometric pressure also affects C_S, and the correction expression is (APHA, 1971):

$$C_s' = C_s\left(\frac{P_b - P_v}{760-P_b}\right) \tag{3-28}$$

where C_s = saturation value at sea level, at the temperature of the water, mg/l

C_s' = corrected value at the altitude of the river, mg/l

P_b = barometric pressure at river altitude, mm Hg

P_v = saturation vapor pressure of water at the river temperature, mm Hg

As an approximation of the influence of altitude, C_s decreases about 7% per 2,000 feet of elevation increase.

Henry's law can also be used to estimate the solubility of dissolved oxygen, usually to within 1-3% of the correct value (Daniels and Alberty, 1967). Henry's law is expressed as:

$$C_S = k_H P_{O_2} \tag{3-29}$$

where k_H = coefficient of absorption, ml/l

p_{O_2} = partial pressure of oxygen, atmospheres

Values for the absorption coefficient are shown in Table 3-9.

TABLE 3-9. SOLUBILITIES OF OXYGEN IN WATER FOR DIFFERENT TEMPERATURES (CRC, 1967)

Temperature °C	Temperature °F	Oxygen Absorption Coefficient, k_H (ml/liter)
0	32	48.9
5	41	42.9
10	50	38.0
15	59	34.2
20	68	31.0
25	77	28.3
30	86	26.1
35	95	24.4
40	104	23.1

The absorption coefficient expresses the volume (in ml at standard pressure) of oxygen dissolved in a liter of water. To convert this volume to mass (as mg) the ideal gas law is used:

$$C_s = \frac{p_{O_2} k_H M}{R_u T} \qquad (3\text{-}30)$$

where M = molecular weight of oxygen (=32)

R_u = universal gas constant, 0.082055 l-atm/gm°K

T = absolute temperature (°K), at which k_H is calculated

3.3.3 Methods of Measurement

Elmore and Hayes (1960) have summarized the work of numerous researchers who have measured dissolved oxygen saturation. According to Elmore and Hayes, Fox in 1909 used a gasometric technique in which a known volume of pure oxygen was exposed to a known volume of water. After equilibrium had been established the volume of oxygen above the water was determined, and the solubility calculated assuming air contained 20.90% oxygen. From the tests an expression was developed for the oxygen absorption coefficient as a function of temperature.

From Fox's expression, Whipple and Whipple (1911) converted their results from milliliters per liter to parts per million. These results were given in Table 3-7.

Truesdale, et al. (1955) used gaseous nitrogen to deoxygenate water samples, and then allowed the water to return to equilibrium conditions. At different time intervals, subsamples were removed and analyzed by an adaptation of the Winkler (1891) procedure.

Morris (1959) conducted a series of 12 experiments under conditions similar to those of Truesdale, et al. (1955). Morris' experiments were conducted under controlled atmospheric conditions and using titrimetric methods. Following that, thirteen more experiments were conducted using a gasometric technique. The results tended to support the findings of Fox.

Then, in 1960, Elmore and Hayes undertook to determine dissolved oxygen saturation values in water. The work was done because of disagreement remaining among researchers. The results of Elmore and Hayes (1960) were summarized earlier in Table 3-8. The procedures they used were similar to the Truesdale group.

The determination of the solubility of oxygen in seawater from 0°C to 35°C and for various chlorinities was done by Green (1965), and discussed by Green and Carritt (1967). Green used a Jocobsen-Worthington equilibrator and a titration method similar to that described by Carpenter (1965).

3.3.4 Summary

Today, significant differences exist among the results obtained by various researchers regarding the "true" value of dissolved oxygen saturation under specified conditions. These discrepancies can be as large as 11 percent for high salinity conditions (compare Table 3-7 with Equation (3-27)). Under conditions of zero salinity, the discrepancies observed are generally less than two percent (compare Table 3-7 and Table 3-8). Knowing the possible ranges of errors in using a particular formulation for C_s permits the user to decide whether they are significant in his study. In instances where the outcome is sensitive to C_s, and only a few values of C_s are needed, it may be justifiable to measure C_s directly rather than to use tabulated values.

3.3.5 References

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3.4 PHOTOSYNTHESIS

3.4.1 Introduction

In simulating the dissolved oxygen resources of aquatic ecosystems, the need frequently arises to include the process of photosynthesis. Simulation of photosynthetic oxygen production can be accomplished in one of two ways. One method is to first model algal growth and then relate oxygen production to the predicted algal growth rate. The second method is simply to include a term for time averaged or instantaneous photosynthetic oxygen production in the dissolved oxygen mass balance equation without simulating algal growth. The latter method, although easier from a modeling standpoint, still requires the estimation of a number of parameters, either by direct measurement from the water body to be simulated, or by the use of previously tabulated values.

3.4.2 Simulating Photosynthetic Oxygen Production

Many investigators have simulated photosynthetic oxygen production rates without modeling algal growth. This section will be limited to a case-by-case discussion of these methods, and will not include algal growth kinetics. For a discussion of algal growth kinetics see Section 3.9.

O'Connell and Thomas (1965) examined photosynthetic oxygen production by benthic algae and rooted aquatic plants in the Truckee River during the months of July, 1962, and August, 1963. O'Connell and Thomas used two methods both of which involved determining net photosynthesis (P-R). In their first method, all terms (other than P-R) were evaluated in an unsteady dissolved oxygen mass balance equation at two hour time increments over a two-day period. Data were collected at a number of locations along the stream. In their mass balance equation, BOD concentrations, BOD decay rate, dissolved oxygen deficits, the reaeration coefficient, and the substantial concentration derivative (defined below) required evaluation. Additionally the researchers included oxygen consumption due to nitrification by finding the stoichiometric quantity of oxygen necessary to oxidize the ammonia and nitrite found to have either been removed from solution or converted to nitrate. The substantial derivative reflects the concentration change that is observed moving downstream at the local stream velocity.

By using a tracer dye, O'Connell and Thomas were able to determine the time of passage of a "slug" of water as it passed from station to station. Their results were such that net P-R for each of a number of locations and at all hours throughout the day could be found. Figure 3-4 illustrates the diurnal P-R variation at one of their stations.

In their second method, O'Connell and Thomas used algal chamber measurements to obtain an independent estimate of the net oxygen change in the stream due to photosynthesis. This method consisted of using plexiglass chambers containing submersible pumps. The chambers were sealed with a sheeting that was oxygen impermeable. The chambers were then placed in the stream and petri dishes, upon which Oscillatoria had been grown, were placed in the chamber. Tests were conducted at various times during the day and night as well as at different locations. Because the test chambers were filled with river water, oxygen was consumed by both carbonaceous and nitrogenous oxygen demanding material as well as plant respiration. Net P-R values were corrected for this sink of oxygen. The outcomes of the two approaches were quite similar, as illustrated by Figure 3-4.

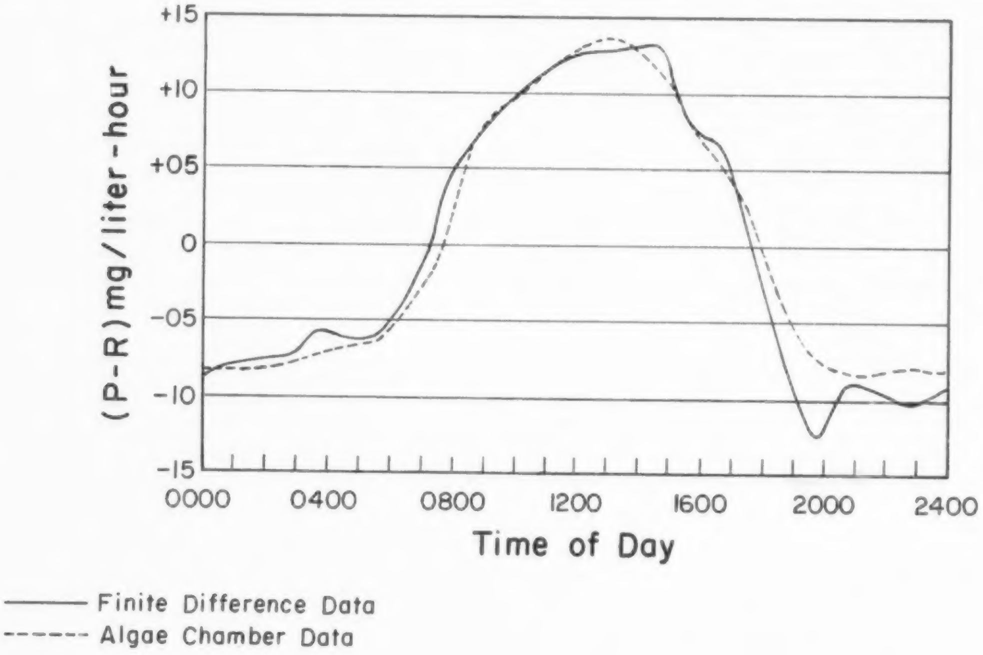

Figure 3-4. Diurnal variation of (P-R) in Truckee River near Station 2B (O'Connell and Thomas, 1965).

O'Connor and Di Toro (1970) have hypothesized what the functional forms might be for photosynthetic oxygen production and for oxygen depletion by respiration. From collected data, they were able to evaluate proportionality constants needed in their expressions. The photosynthetic expression was assumed to be time-dependent, while that for respiration was assumed time-independent. Based upon the results of earlier studies (Westlake, undated) O'Connor and Di Toro assumed that the photosynthetic oxygen production rate, averaged over depth, would resemble the diurnal incident solar radiation curve. For the sake of simplicity, O'Connor and Di Toro also assumed that the photosynthetic oxygen production curve, P(t), could be represented by a half cycle sine wave:

$$P(t) = \begin{cases} P_m \sin \left[\frac{\pi}{p}\left(t-t_s\right)\right] & \text{when } t_s < t < t_s + p \\ 0 \text{ when } t \leq t_s \text{ or } t \geq t_s + p \end{cases} \tag{3-31}$$

where P_m = maximum rate of photosynthetic oxygen production, mg/l-day

t = current time, expressed as a fraction of a day

t_s = the time of day representing sunup, expressed as a fraction of a day

p = daylight fraction of the day

Since this function was assumed to have a period of one day, its periodic extension could be expressed as a Fourier Series (not discussed here).

In Equation (3-31) both t_s and p are established using the times of sunrise and sunset. O'Connor and Di Toro found that the best fits to their data were obtained if t_s was slightly later than sunrise and p was slightly less than the total time between sunrise and sunset. It remained then to quantify P_m and R (respiration). O'Connor and Di Toro adopted a heuristic approach, based primarily on the diurnal fluctuation at various stations downstream and guided by whatever qualitative information was available about the algal populations involved. Calculations were carried out on the Grand, Clinton, Truckee, Ivel, and Flint Rivers. The resulting formulations agreed reasonably well with observations on these streams. Weeter and Bell (1971) have used a modification of O'Connor and Di Toro's model. Their approach was verified on the Wabash River, Indiana, and found to agree well with observed data.

Both of the methods described above for finding instantaneous production rates (O'Connell and Thomas, 1965; and O'Connor and Di Toro, 1970) can be used to find the net average photosynthetic oxygen production over a day. In the first method net P-R is determined by finding the area under the P-R versus time curve, such as the curve that was shown in Figure 3-4. The net production is not zero since the total daytime production is greater than the total nighttime consumption.

From O'Connor and Di Toro's methods, average daily photosynthesis (P_{av}, mg/l-day) is given by integrating Equation (3-31) over 24 hours, giving:

$$P_{av} = 2p\, P_m / \pi \qquad (3\text{-}32)$$

Kelly, et al. (1975) have described a method also applicable to streams where the net photosynthetic oxygen production rate (P-R) is expressed as a Fourier cosine series. A period of 48 hours was used so that values at the beginning and end of a day were not constrained to be identical. Their problem reduced to determining enough Fourier coefficients so that a finite number of terms could accurately represent P-R.

Their method used digitally recorded diurnal oxygen concentration changes to solve for the coefficients in an oxygen mass-balance equation. Data were recorded at two stations on a river and the unknown coefficients were selected so that the downstream values were accurately predicted from the upstream values. A unique feature of this work is that Kelly, et al. developed an error analysis procedure applicable to their method.

In the work just described on stream photosynthesis, neither researcher explicitly included light intensity in their expressions. For deeper bodies of water, such as impoundments, inclusion of this term along with an extinction coefficient is necessary. Such an expression is given by (U.S. EPA, 1976):

$$\frac{P_{av}}{P_s} = \frac{2.718\, f}{K_e H\, T_p} \left(e^{-\alpha I_a / I_s} - e^{-I_a / I_s} \right) \qquad (3\text{-}33)$$

where $\alpha = e^{-K_e H}$

P_{av} = average daily algal oxygen production rate, mg/l-day

P_s = the light saturated rate of oxygen production, mg/l-day

I_a = the average light intensity during the daylight portion of the day (any units consistent with those chosen for I_s)

I_s = the light saturated intensity (optimum light intensity for growth)

f = the number of hours of daylight, per day

T_p = twenty-four hours

K_e = the extinction coefficient, 1/m

H = depth, m

The following range was suggested for the extinction coefficient:

0.1-0.5/m for very clear impoundments,

0.5-2.5/m for moderately turbid waters, and

2.5/m or greater for very turbid waters

The U.S. EPA suggested that P_s was related to the chlorophyll-a concentration as follows:

$$P_s = 0.25\ \mathrm{Chl}_a \qquad (3\text{-}34)$$

where Chl_a = chlorophyll-a concentration, μg/l

The U.S. EPA also suggested an expression for predicting respiration, R, as a function of chlorophyll-a concentration:

$$R = r \cdot \mathrm{Chl}_a \qquad (3\text{-}35)$$

where R = mg oxygen utilized/l-day

Chl_a = chlorophyll-a concentration in μg/l

r = constant ranging from 0.005 to 0.030 with 0.025 a common value. This corresponds to a 10 to 1 ratio of P_s to R

The respiration rate is known to vary considerably and depends on the nutrient concentration and age of the culture. Hence the average daily algal respiration calculated from equation (3-35) is subject to some degree of uncertainty.

Bailey (1970) also developed an expression for gross photosynthesis (in the Sacramento-San Joaquin estuary) that included a light limitation term. It is:

$$P_{av} = 3.16\ \mathrm{chl}\ {\frac{I}{k_e}}^{0.667} + 0.16T - 0.56H \qquad (3\text{-}36)$$

where P_{av} = average daily gross photosynthetic rate, mg/l-day

I = mean daily solar intensity, cal/sq.cm-day

k_e = light extinction coefficient, m^{-1}

T = mean temperature, °C

H = mean water depth, m

chl = mean chlorophyll, mg/l

The multiple correlation coefficient obtained in developing Equation (3-36) was 0.96. This means that 96^2 or 92 percent of observed variability of P_{av} could be accounted for by I, k_e, T, H, and chlorophyll concentration with this form of equation.

3.4.3 Tabulated Values for Photosynthesis

Table 3-10 shows values of gross average photosynthetic oxygen production and average respiration for several waterbodies. These values are expressed on an areal basis. To convert from an areal basis to mg/l-day in vertically well-mixed systems, divide the areal rate (gm/sq.m-day) by the average depth (in meters).

TABLE 3-10. SOME AVERAGE VALUES OF GROSS PHOTOSYNTHETIC PRODUCTION OF DISSOLVED OXYGEN AND AVERAGE RESPIRATION (AFTER THOMANN, 1972, AND THOMAS AND O'CONNELL, 1966)

Water Type	Average Gross Production (gm/m^2-day)	Average Respiration (gm/m^2-day)
Truckee River - Bottom attached algae	9	11.4
Tidal Creek - Diatom Bloom (62-100x10^6 diatoms/l)	6	
Delaware Estuary - summer	3-7	
Duwamish River Estuary - Seattle, Washington	0.5-2.0	
Neuse River System - North Carolina	0.3-2.4	
River Ivel	3.2-17.6	6.7-15.4
North Carolina Streams	9.8	21.5
Laboratory Streams	3.4-4.0	2.4-2.9

The use of Equations (3-34) and (3-36) depend on estimates of chlorophyll-a concentrations. Table 3-11 presents chlorophyll-a values on an areal basis for various communities. Also presented in that table are assimilation numbers, defined as grams of oxygen produced per hour per gram of chlorophyll-a. Hence by estimating the chlorophyll-a concentration the maximum oxygen production rate can also be estimated. Equation (3-34) is an example of an application of this concept.

TABLE 3-11. CHLOROPHYLL-a AND ASSIMILATION NUMBER OF VARIOUS COMMUNITIES (AFTER ODUM, *et al*., 1958)

Plankton Communities	Euphotic Zone* Chlorophyll-a gm/m^2	Assimilation Number, gm Oxygen Per Hour Per gm Chlorophyll-a
Not including bottom plants:		
Long Island Sound	0.1-0.6	1.3
Diatom bloom, Moriches Bay one meter	0.20	4.5
Sewage Pond, Kadoka, S.D.	1.5	2.
Shallow Aquatic Communities with Bottom Plants:		
Rocky Mountain Stream, Utah	0.3-1.6	0.7-2.0
Blue-green algal mat, polluted stream, Mission River, Texas, August, 1957	2.5	-

*From the surface to the depth where light intensity = 1% of surface light.

3.4.4 Summary

Of the methods presented here for simulating photosynthetic oxygen production, all but one (O'Connell and Thomas, 1965) provide quantitative relationships. All of the relationships require the user to make estimates of several parameters, such as the maximum rate of photosynthesis. Many of the measurement techniques used by the researchers described depend on determining, in the dissolved oxygen mass balance equation, all terms other than P-R, from which P-R can then be determined. Inherent in this procedure is the hazard of incorporating errors due to errors in estimating values of the required parameters, such as the deoxygenation rate, k_d. Even the use of tabulated values of dissolved oxygen saturation, as described in Section 3.3, can produce erroneous results. Direct measurement techniques, such as the light and dark chambers method, can offer an advantage in this respect (see Thomas and O'Connell (1966) and McIntyre, et al. (1964) for applications). However, this method has a disadvantage in that it only samples at one point, and also disturbs the algal population and surrounding flow field.

Several of the equations presented here (Equations (3-34), (3-35), and (3-36) require chlorophyll concentration measurements. Table 3-11 has presented only a limited amount of data on chlorophyll-a concentrations. Also chlorophyll-a concentrations are not constant, although over a relatively short time period, chlorophyll may be modeled as such. Each of the expressions for photosynthesis that contain terms for chlorophyll predict daily average rates, and not instantaneous rates. It would generally be inappropriate to use either of these expressions in a model with a time step shorter than one day, except to approximate diurnal dissolved oxygen ranges that might be expected given typical chlorophyll concentrations.

3.4.5 References

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3.5 CARBONACEOUS DEOXYGENATION

3.5.1 Introduction

Biochemical oxygen demand (BOD) is the oxygen consumed by microorganisms utilizing organic matter as food and breaking down the complex compounds into simpler products. This process can be divided into two stages: the first being due to oxidation of carbonaceous matter and the second due to nitrogenous substance oxidation. Only carbonaceous oxidation is described here; oxidation of nitrogenous matter is discussed in Section 3.6.

The amount of BOD present in an aquatic system has traditionally been measured by applying the standard BOD_5 test to a water sample. Appropriate factors are available which can then be applied to the 5-day BOD values in order to obtain the ultimate first stage oxygen demand. These factors vary from 1.10 to 2.40 with 1.45 being the most common (i.e., ultimate BOD = 1.45 BOD_5) (Crim and Lovelace, 1973).

In addition to externally applied loads of BOD such as those entering the system from a sewage treatment facility, the amount of BOD present in a system may also be affected by the following internal sources: 1) the death of algae, zooplankton, fish and bacteria, 2) excretions by algae, zooplankton, fish and bacteria, and 3) benthal demands.

The BOD decay process can be described by the following expression:

$$\text{SUBSTRATE} + \text{BACTERIA} + O_2 + \underset{\text{(NUTRIENTS)}}{\text{GROWTH FACTORS}} \longrightarrow$$

$$CO_2 + H_2O + \text{MORE BACTERIA} + \text{ENERGY}$$

At present virtually all investigators assume some form of first order reaction to describe the kinetics of BOD exertion. Typically the BOD expression is represented as:

$$\frac{\partial L}{\partial t} = k_d L \qquad (3\text{-}37)$$

where L = BOD remaining at time t, mg/l

k_d = deoxygenation coefficient, day^{-1}

In the discussion that follows, it will be necessary to distinguish between different but related BOD decay rates. The following convention will be followed:

k_d = receiving water deoxygenation rate due to BOD exertion,

k_1 = laboratory deoxygenation rate due to BOD exertion, and

k_r = receiving water exertion rate of BOD (includes all sinks of BOD, including deoxygenation and settling).

Some attempts have been made to develop relationships between these rates, as will be discussed later.

3.5.2 Factors Affecting Deoxygenation Rates

Many factors are known to influence both the deoxygenation rate, k_d, and the disappearance rate of BOD, k_r. Those to be discussed are:

- temperature
- hydraulic parameters
- degree of waste treatment, and
- other *in situ* physicochemical processes.

The most commonly used temperature correction expression for k_d is of the following form:

$$k_d = \left(k_d\right)_{20} \theta^{T-20} \qquad (3\text{-}38)$$

where k_d = deoxygenation rate at temperature T (°C), day^{-1}

$(k_d)_{20}$ = deoxygenation rate at 20°C, day^{-1}

θ = temperature correction coefficient

Values reported by modelers for the temperature coefficient are shown in Table 3-12. Also included in that table are the deoxygenation coefficients used in the studies.

TABLE 3-12. VALUES OF TEMPERATURE CORRECTION FACTOR, θ AND DEOXYGENATION COEFFICIENT, k_d

Location	Deoxygenation Coefficient, k_d at 20°C, day^{-1} (base e)	Temperature Coefficient, θ	Reference
--	0.1 - 2.5	1.02 - 1.09	Baca and Arnett, 1976
N. Fork Kings River, California	0.2	--	Tetra Tech, 1976a
--	0.1 - 1.5	--	Hydrologic Engineering Center, 1974
Lake Washington	0.2	--	Chen and Orlob, 1975
--	0.06 - 0.36	1.075	Lombardo, 1972
Merrimack River	0.01 - 0.1	--	Camp, 1965
--	0.2 - 2.0	--	Hydroscience, 1971
Boise River, Idaho	0.25	1.047	Chen and Wells, 1975
San Francisco Bay Estuary	0.2	1.047	Chen, 1970
--	0.2	--	Thomann, et al., 1974
--	0.1 - 0.3	--	Tetra Tech, 1976b
--	0.23	1.05	Crim and Lovelace, 1973

Bansal (1975) has investigated the effects of various hydraulic parameters on k_d by combining these parameters into dimensionless groups and then, by using historical data, employing regression methods to develop relationships between the groups. He chose various combinations of parameters, and that combination yielding the best results is shown in Figure 3-5. The data points from which the line of best fit was developed are not included on the figure; however the predictive formulation is, including the correlation coefficient and the standard error of estimate.

The data Bansal (1975) used in his work are presented in Table 3-13. From his work Bansal concluded that the ratio of Reynolds number to Froude number offered the best method (with respect to those parameter combinations he evaluated) of predicting k_d independently of stream location, pollution load, and channel configuration. The effect of temperature is implicitly included in the Reynolds number. This temperature influence is that affecting water density and viscosity, and not microbial activity, as expressed by Equation (3-38). It is more meaningful to incorporate the effects of

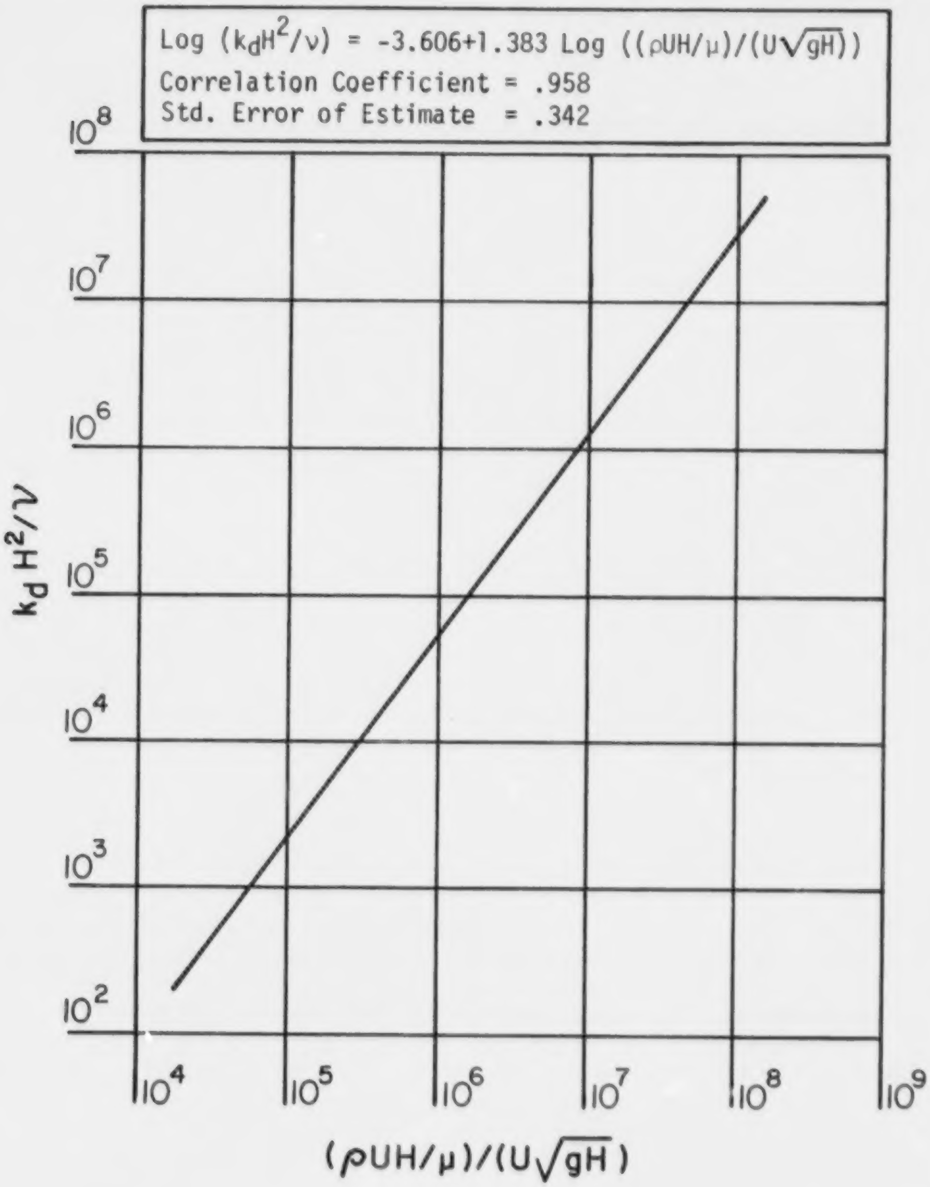

Figure 3-5. Deoxygenation parameter $(k_d H^2/\nu)$ versus the Reynolds Number and Froude Number $(\rho UH/\mu)/(U\sqrt{gH})$ (from Bansal, 1975).

TABLE 3-13. DEOXYGENATION RATE CONSTANTS (FROM BANSAL, 1975)

Discharge cfs	Cross-sectional Area sq.ft.	Top Width ft.	Temp. °C	k_d Observed
Kansas River at Bonner Springs, Kansas				
15,200	4,300	770	25	.02
2,160	1,200	505	28	.12
2,090	1,170	500	25	.12
2,440	1,300	525	24	.24
1,300	850	450	9	.02
828	550	415	5	.16
632	425	405	9	.26
1,080	710	432	14	.17
Kansas River at Lecompton, Kansas				
1,750	750	725	27	.19
1,360	590	660	32	.15
2,060	880	774	28	.35
2,300	1,000	757	10	.30
1,040	450	592	6	.47
793	350	538	0	.23
1,170	500	620	16	.05
Kansas River at Topeka, Kansas				
3,040	1,450	468	22	.08
1,460	700	437	31	.07
1,800	865	447	27	.1
2,690	1,285	466	18	.37
1,900	910	450	7	.14
764	365	405	7	.06
631	310	368	11	.23
608	290	364	15	.10
Republic River below Milford, Kansas				
258	184	196	24	.18
657	412	251	28	.19
609	392	249	24	.07
201	140	166	14	.25
15	10	68	1	.14
36	26	77	0	.23
249	177	192	16	.29

(continued)

TABLE 3-13 (continued)

Discharge cfs	Cross-sectional Area sq.ft.	Top Width ft.	Temp. °C	k_d Observed
Smoky Hill River at Enterprise, Kansas				
215	122	119	27	.09
100	57	69	32	.26
373	211	131	24	.16
146	83	91	6	.32
113	65	75	0	.14
210	120	118	15	.17
157	88	97	14	.24
Smoky Hill River at New Cambridge, Kansas				
185	87	86	27	.09
67	35	79	31	.19
734	252	88	29	.27
Solomon River at Niles, Kansas				
61	65	53	28	.21
35	40	49	30	.19
117	125	61	21	.06
Kansas River at Wamego, Kansas				
890	390	413	27	.23
1,540	670	468	26	.13
2,530	1,080	540	27	.30
1,470	730	462	15	.26
680	300	395	0	.28
535	225	381	2	.11
483	190	375	7	.06
Big Blue River at Tuttle Creek, Kansas				
1,060	1,050	194	22	.21
162	70	76	24	.14
90	42	62	27	.23
810	490	191	23	.28
961	1,000	194	8	.6
232	108	92	1	.37
50	30	52	6	.15
50	30	52	13	.2

(continued)

TABLE 3-13 (continued)

Discharge cfs	Cross-sectional Area sq.ft.	Top Width ft.	Temp. °C	k_d Observed
Kansas River at Manhattan (Fort Riley), Kansas				
1,250	4,250	533	26	.26
559	1,750	493	32	.15
1,200	4,050	530	26	.10
511	367	247	25	.09
Solomon River at Glen Elder, Kansas				
44	38	49	28	.20
47	40	49	28	.23
79	58	53	24	.10
30	30	33	7	.35
48	41	49	0	.34
33	31	36	0	.37
30	30	33	5	.35
Saline River at Tescott, Kansas				
8.3	14	19.4	2.7	.37
5.8	10	17.8	28	.25
132	75	30	21	.26
Smoky Hill River at Mentor, Kansas				
138	88	83	24	.10
35	20	81.5	26	.15
675	288	92.5	26	.42
Smoky Hill River at Langley, Kansas				
77	60	57	23	.42
147	85	67	27	.51
493	210	90	24	.14
249	122	75	23	.14
14	15	20	7	.20
21	21	23	1	.28
18	19	22	6	.29
81	60	58	11	.33
Grand River, Michigan				
295	320	168.4	20	.59

(continued)

TABLE 3-13 (continued)

Discharge cfs	Cross-sectional Area sq.ft.	Top Width ft.	Temp. °C	k_d Observed
Clinton River, Michigan				
33	44.6	28.22	20	3.37
Truckee River, Nevada				
180	150	89.8	20	.36
195	150	89.8	20	.36
271	150	89.8	20	.96
Flint River, Michigan				
134	210	100	--	.56
174	200	76.9	20	.63
174	400	153.8	20	.69
204	296	170.6	20	.69
204	400	210.5	20	.69
Jackson River, Virginia				
100	365	122	20	1.25
North Branch Potomac River (Maryland, West Virginia)				
100	100	50	20	.4
North Branch Susquehanna				
1,000	1,700	425	20	.35
New River, Virginia				
1,200	1,720	344	20	.5
Upper Hudson, Troy, New York				
3,000	6,000	343	20	.125
4,500	6,750	321	20	.165
Lower Sacramento River				
10,000	8,000	457	20	.4

(continued)

TABLE 3-13 (continued)

Discharge cfs	Cross-sectional Area sq.ft.	Top Width ft.	Temp. °C	k_d Observed
Upper James River, Virginia				
1,800	8,000	742	20	.48
2,600	11,500	935.5	20	.30
9,000	14,500	935.5	20	.31
7,500	14,000	903.2	20	.41
4,500	14,500	935.2	20	.39
3,800	13,500	871	20	.38
1,350	15,000	967.7	20	.43
Cooper River, South Carolina				
10,000	40,000	1,000	20	.3
Savannah River, Georgia and South Carolina				
7,000	10,000	1,000	20	.3
6,800	40,000	1,428.6	20	.3
South New Jersey				
23	2,500	208.3	20	.2
Compton Creek, New Jersey				
10	1,000	69	20	.23
10	790	75	20	.23

temperature by using Bansal's expression to evaluate k_d at some base temperature, and then use Equation (3-38) to correct for temperature variations from the base temperature.

Tables 3-4 and 3-6, previously presented in Section 3.2.4 on reaeration, also contain a number of deoxygenation coefficients. Table 3-17 in Section 3.6 on nitrogenous oxidation contains additional k_d values.

Hydroscience (1971) has developed a relationship for predicting k_d in streams and rivers that takes into account both stream depth and degree of waste treatment. This relationship, developed from data surveys conducted by Hydroscience, is graphically shown in Figure 3-6. Data points are not included in the figure. The dependency of k_d on bottom configuration reflects the importance of attached organisms in contributing to the deoxygenation process.

Also, as discussed by Hydroscience, the nature of the residual organic matter in the effluent of upstream sewage treatment plants should be considered when estimating k_d. A significant portion of the waste material may be residual bacterial cells, since most of the complex organic matter in the raw waste is stabilized by treatment processes. The lower limit shown in Figure 3-6 represents highly treated, well oxidized effluents having a stable residual organic component. The upper limit is representative of less highly treated wastes, with higher values of ammonia present. The middle curve is representative of treatment processes with some nitrification.

As previously mentioned, in some streams, rivers, and estuaries, there may be a difference between the deoxygenation rate, k_d, and the BOD removal rate, k_r. The following factors are known to contribute to such differences (Eckenfelder and O'Connor, 1961):

1. Sedimentation and flocculation: organic matter may settle, which decreases the amount of suspended BOD.

2. Scour: settled organic matter may be resuspended by high velocity flow and add to the water column BOD concentration.

3. Volatilization and Reaction: certain organic compounds may react with compounds in the benthos and escape as gases (e.g., hydrogen sulfide, methane).

4. Mixing: increased mixing has been found to increase the deoxygenation rate.

Table 3-14 provides a comparison between k_d and k_r for several streams (Eckenfelder and O'Connor, 1961).

Bosko (1966), as discussed by Tierney and Young (1974) developed a relationship between k_d and k_1. It is given by:

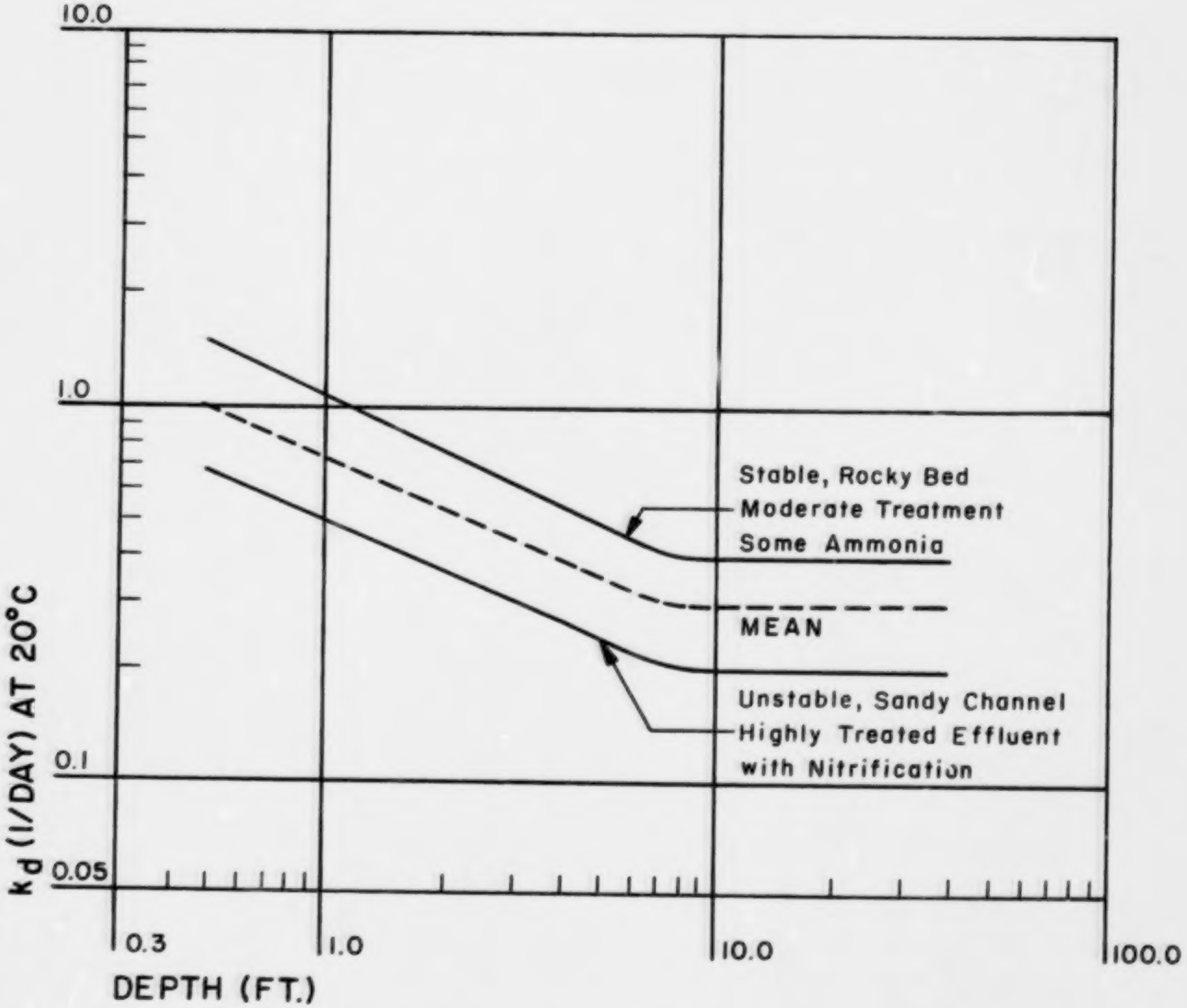

Figure 3-6. Deoxygenation coefficient as a function of depth (after Hydroscience, 1971).

TABLE 3-14. DEOXYGENATION RATES FOR SOME SELECTED RIVERS (ECKENFELDER AND O'CONNOR, 1961)

River	Flow (cfs)	Temp. (°C)	BOD_5 (mg/l)	k_d (day^{-1})	k_r (day^{-1})
Elk	5	12	52	3.0	3.0
Hudson	620	22	13	0.15	1.7
Wabash	2800	25	14	0.3	0.75
Willamette	3800	22	4	0.2	1.0
Clinton	33	--	--	.14-.23	2.5
Tittabawassee	--	--	--	0.05	0.5

$$k_d = k_1 + n\ (V/D) \qquad (3\text{-}39)$$

where k_d = stream deoxygenation rate coefficient, base e, day^{-1}

k_1 = laboratory deoxygenation rate coefficient, base e, day^{-1}

V = stream velocity, ft/sec

D = stream depth, feet

n = coefficient of bed activity

The second term on the right side of Equation (3-39) and the values of n in Table 3-15 reflect the importance of organisms in the stream bed that utilize BOD.

The coefficient n is taken as a step function of stream slope, as shown in Table 3-15 below.

Several investigators have modified the traditional BOD decay formulation, Equation (3-37) to account for several other phenomena. In an attempt to better represent internal sources of BOD in addition to the externally applied loads, Baca and Arnett (1976) proposed the following formulation:

TABLE 3-15. CHANGES IN COEFFICIENT OF BED ACTIVITIES BY STREAM SLOPE

Stream Slope (ft/mi)	n
2.5	.1
5.0	.15
10.0	.25
25.0	.4
50.0	.6

$$\partial L/\partial t = -k_1 L + \alpha\left(F_p P + F_z Z\right) \quad (3\text{-}40)$$

where L = concentration of BOD, mg/l

α = stoichiometric constant, mg-O_2/mg-C

F_z = death rate of zooplankton due to fish predation, day^{-1}

F_p = death rate of phytoplankton due to zooplankton predation, day^{-1}

P = phytoplankton concentration, mg/l

Z = zooplankton concentration, mg/l

Thomas (1948) introduced the concept that the river removal rate, k_r, could be defined as the sum of a laboratory coefficient, k_1, and an additional coefficient, k_3, that would account for additional BOD removal due to factors such as sedimentation, scour, flocculation, and volatilization occurring in benthal deposits.

Baca and Arnett (1976) incorporated a similar concept into their BOD formulation for the Gray's Harbor/Chehalis River study. Their expression has the following form:

$$\partial L/\partial t = -\left(k_1 + k_3\right)L + P \quad (3\text{-}41)$$

where L = ultimate BOD, mg/l

k_1 = laboratory deoxygenation coefficient; typically 0.1-0.8/day

k_3 = "sedimentation" coefficient; typically 0.0-3.5/day

P = scour coefficient; typically 0.0-0.8 mg/l-day

Orlob (1974) is another investigator who has used the sedimentation coefficient in his work.

3.5.3 Measurement of BOD Decay Rate

The removal rate of BOD from receiving water can be determined indirectly from in situ BOD measurements by using the BOD mass-balance equation to solve for the removal rate. There are three aspects of this approach that should be considered:

1. The removal rate so obtained may approximate either k_r or k_d. If filtered BOD samples are taken and the settleable fraction of BOD is not assumed to represent a significant demand on oxygen resources, then k_d is obtained. If total BOD is sampled then k_r is obtained.
2. This method is limited to cases where sufficient data are available, or can be generated, to perform the necessary calculations in the mass-balance equation used.
3. The method is usually applicable in "idealized" situations where the mass-balance equation can be explicitly solved for k_r (or k_d). In many situations, the assumptions required to reduce the mass-balance equation to such a simplified form may not be justifiable.

Three illustrations of this technique will be shown here, two applicable to streams, and one to tidally influenced rivers. Each method entails the use of a plot.

For the first method, the stream should have a relatively constant cross section, constant flow rate, and a BOD loading located at a position that will be called x = 0. The BOD concentration can then be expressed as:

$$L = L_o \exp\left(\frac{-k_r x}{U}\right) \tag{3-42}$$

where U = mean stream velocity

x = distance downstream from BOD source

L_o = BOD concentration at x=o (just below source)

Plotting the log of BOD concentration (BOD_5 or $BOD_{ult.}$) versus distance should produce a generally straight line with slope of $-k_r/U$. An example plot is shown in Figure 3-7. Care must be exercised to convert the slope from base 10 logarithms as given in the semi-log plot to base e logarithms. This conversion is accomplished by multiplying the k_r value in base 10 logarithms by 2.3, as shown in the figure.

The second illustration is similar to the first, except that a uniform inflow of water occurs along the reach. Otherwise the assumptions for the two illustrations are the same. The uniform inflow is assumed to be free of BOD. The mass-balance equation then is:

$$L = L_o \left(\frac{Q_o}{Q} \right)^a \qquad (3\text{-}43)$$

where Q_o = flow rate at $x = 0$

$Q = Q_o + (\Delta Q)\,x$, flow rate at a distance x

$a = \dfrac{k_r A_o + \Delta Q}{\Delta Q}$

A_o = stream cross-sectional area = Q_o/U_o

U_o = stream velocity at $x = 0$

ΔQ = incremental flow per unit of distance (assumed constant over the reach under consideration)

For this case a log-log plot of BOD and flow rate, Q, should be developed. The slope of the plot will be -a. From the known A_o and ΔQ, k_r can be obtained directly. Note that k_r need not be converted from base 10 logarithms to base e, as it already is to the base e.

For tidally influenced rivers where the same assumptions hold as in the first illustration above, BOD concentration can be expressed as a function of distance, x, from the discharge point by:

$$L = L_o \exp\left(j_1 x \right),\ x < 0 \text{ (in upstream direction)} \qquad (3\text{-}44)$$

$$L = L_o \exp\left(j_2 x \right),\ x > 0 \text{ (in downstream direction)} \qquad (3\text{-}45)$$

$$j_1 = \frac{U}{2E} \left[1 + \sqrt{1 + \frac{4k_r E}{U^2}} \right] \qquad (3\text{-}46)$$

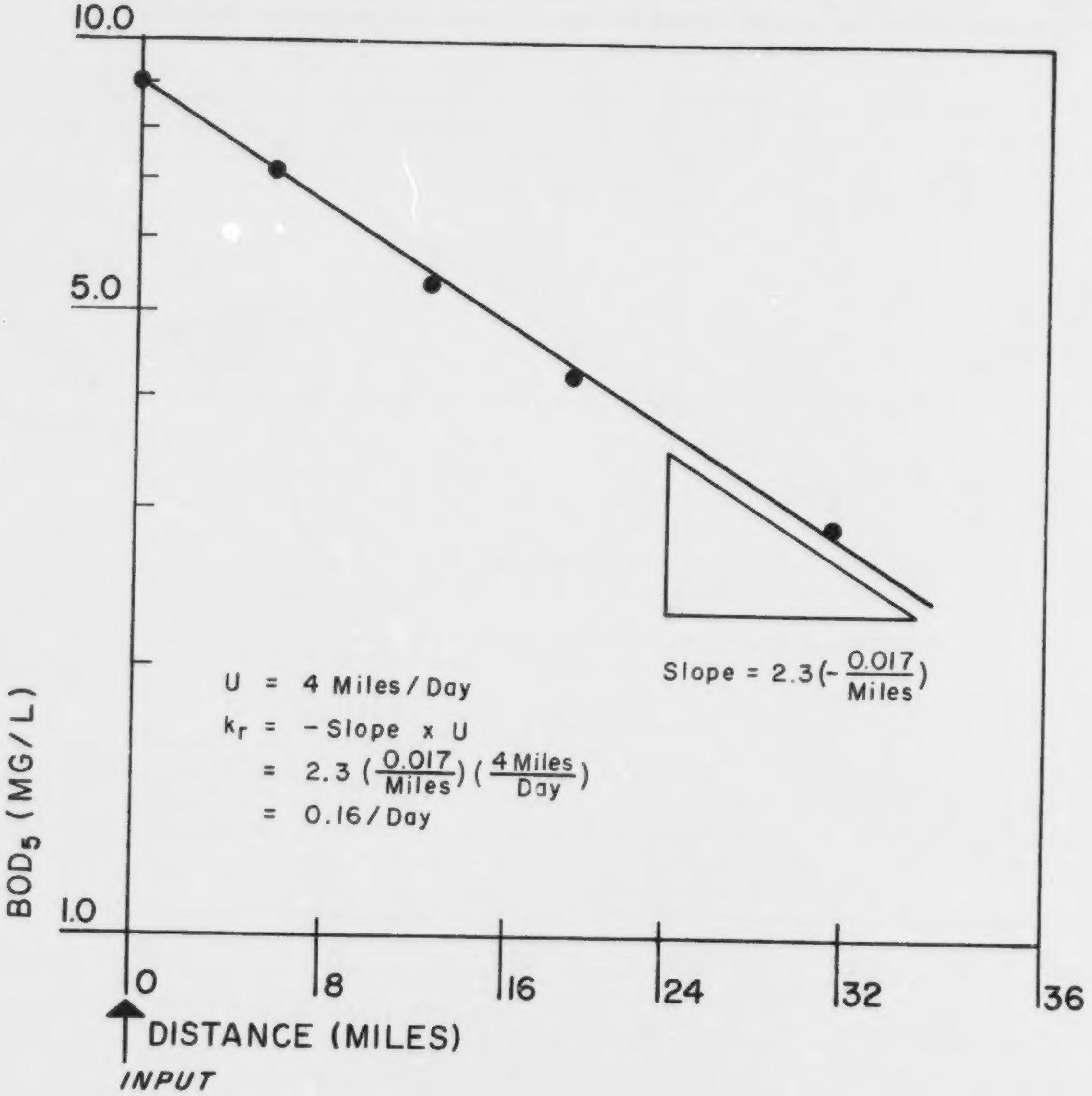

Figure 3-7. Example of computation of k_r from stream data (from Hydroscience, 1971).

$$j_2 = \frac{U}{2E}\left[1 - \sqrt{1 - \frac{4k_r E}{U^2}}\right] \qquad (3\text{-}47)$$

where E = tidally averaged dispersion coefficient

U = net tidal velocity

By plotting the log of BOD versus distance upstream or downstream, the slope of the plot becomes j_1 or j_2 respectively, and k_r can then be obtained. If the abscissa is distance upstream, then x should be negative and j_1 positive. If the abscissa is distance downstream, then x is positive and j_2 negative.

From laboratory measurements of BOD exerted versus time, various techniques can be used to obtain the BOD decay rate, k_1, where this decay rate is the laboratory decay rate. From the collected data, k_1 can be obtained by one of the five methods described in Nemerow (1974):

1. least-squares technique,
2. slope-method,
3. moments method,
4. logarithmic method, and
5. Rhame's two-point method.

Nemerow also describes an additional laboratory procedure which he uses. Gaudy, et al. (1967) provides further background on these methods.

Using data from the Clinton and Tittabawassee Rivers, Gannon (1966) has compared the many methods of k_1 prediction and has suggested that the Reed-Theriault method (Theriault, 1927) may be superior.

Standard Methods (APHA, 1971) describes an empirical bottle test for determining BOD. Care must be exercised in comparing these BOD values to those which might be observed in surface waters, however. As stated in Standard Methods:

> "The test is of limited value in measuring the actual oxygen demand of surface waters, and the extrapolation of test results to actual stream oxygen demands is highly questionable, since the laboratory environment does not reproduce stream conditions, particularly as related to temperature, sunlight, biological population, water movement and oxygen concentration."

As a corollary to this comment, the decay rates (laboratory versus instream) would not be expected to be identical. Tierney and Young (1974) have addressed this question, as previously discussed, and derived an expression relating k_1 and k_d (Equation (3-39)) applicable to streams.

3.5.4 Summary

As yet, no unified theory has evolved for predicting deoxygenation rates of receiving waters. There are even arguments that the first order decay rate is invalid (Flegal and Schroeder, 1976). Further, the literature, at times, fails to state whether measured BOD rates are k_d or k_r. As noted earlier (Table 3-14), this difference can be substantial, producing differences of as much as an order of magnitude. Tacit adoption of the higher value as the rate of oxygen consumption could produce an underestimate of the dissolved oxygen resources of the receiving water.

One of the more common measurement techniques found in the literature for determining the deoxygenation coefficient in streams is to plot BOD remaining versus distance (or equivalently, versus travel time). However, researchers do not always specify just how the BOD samples were measured, e.g., whether filtered or unfiltered BOD samples were used. Which was used determines if k_d or k_r has been estimated. Also, before using this technique, the user should take care to ascertain whether the assumptions regarding the development of the mass balance equation used are reasonable.

Preliminary stream surveys of reaches to be modeled may be of use to the modeler by qualitatively helping to explain differences in k_r, k_d, and k_1. To quantify such differences, the modeler needs to keep in mind how each rate parameter was obtained, what rate is actually being measured, what phenomena are included, and which are being excluded. For example, the presence on the bottom of streams of colonies of *Sphaerotilus natans* can substantially increase k_d over k_1. Settling of oxidizable material can likewise increase k_r over k_d.

If the BOD decay rate cannot be measured directly, but if the modeler wants an estimate of k_d, the relationships presented earlier between receiving water hydraulic parameters and k_d can be used. Or, for a receiving water body with characteristics approximating one of those tabulated in Tables 3-4, 3-6, 3-13, and 3-17, one may make an estimate. In either case the modeler should be aware that only hydraulic similarities between the tabulated water body and the water body to be modeled are being considered. One can apply Equation (3-38), however, to incorporate a temperature correction for the temperature(s) of interest. The temperature correction expression, Equation (3-38) is a widely accepted method of quantitatively expressing the relationship between k_d and temperature. In most cases this relationship is derived for a limited temperature range. Outside of this range (usually 10°C to 30°C) the relationship will almost certainly produce misleading results.

3.5.5 References

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3.6 NITROGENOUS DEOXYGENATION

3.6.1 Introduction

The rate parameter that is used in simulating nitrification (the oxidation of reduced forms of nitrogen) as a first order, single stage process is commonly denoted as k_n and most often is expressed in units of day^{-1}. This representation of the nitrification process is shown in Equation (3-48):

$$\frac{\partial N}{\partial t} = -k_n N \qquad (3\text{-}48)$$

where N = total oxidizable nitrogen, mg/l

k_n = first order decay rate, day^{-1}

Many other methods of simulating the nitrification process have been used and were briefly discussed in Section 2.5.1. The present section will deal with the rate constant k_n and will discuss variables that affect nitrification as well as methods that have been used to measure k_n. Finally, values of k_n, as found in the literature, will be presented.

As shown in Equation (3-48), using the single stage formulation for simulating nitrification requires values of total oxidizable nitrogen (TON) as well as k_n. Generally TON is taken as the sum of ammonia-nitrogen and organic-nitrogen, although some researchers have chosen to use only ammonia-nitrogen. To compute the oxygen demand resulting from nitrification, the TON is typically multiplied by 4.57, the number of grams of oxygen required to oxidize one gram of ammonia-nitrogen to nitrate. This figure is computed by using the half reaction oxidation-reduction equations for nitrification (presented earlier in Section 2.5.1). In reality, however, some oxygen required in the nitrification process can be obtained through inorganic carbon sources, reducing the total oxygen demand slightly from that estimated by using the half reaction equations. The amount of reduction depends upon the biochemical and nutritional status of the cell. Nitrification synthesis-oxidation equations used by Adams and Eckenfelder (1977) resulted in a value of 4.33 grams of oxygen for the complete oxidation of one gram of ammonia nitrogen.

3.6.2 Factors Which Affect Nitrification

Several environmental factors have been shown to influence the rate at which nitrification occurs. Among them are pH, temperature, suspended particle concentrations, hydraulic parameters, and the benthos of the receiving waters. These factors will be discussed in this section.

A number of researchers (Meyerhof (1917), Engel and Alexander (1958), and Wild, *et al*. (1971)) have studied the effects of pH on nitrification. Meyerhof found the optimum pH for ammonia nitrification to be about 8.6. He also found that at pH values of 7.9 and 9.3 the rate decreases to 50 percent of the maximum. Although Wild, *et al*. found nearly the same optimum pH (8.4), the pH values at which the rate had decreased to 50 percent represented a wider pH range, specifically, 7.1 to 9.8. Engel and Alexander found, contrary to the results of Meyerhof and of Wild, *et al*., that the nitrification rate formed a plateau from pH 7.0 to 9.0 where the rate everywhere within this range was at least 95 percent of the maximum. Outside of this range the rate of nitrification rapidly decreased.

Meyerhof (1916) also investigated the rate of nitrite oxidation and found optimum pH values to be between 8.5 and 9.0. This result is substantiated by Kholdebarin and Oertli (1977b) who found the optimum rate of nitrite oxidation in the Whitewater River to be at pH 8.5.

Researchers have generally found temperature to strongly affect nitrification rates. Although most investigators have found that at a nominal temperature of 20°C, a 10°C temperature change produces a large change in the rate of nitrification, at least one researcher (Borchardt,

1966) found that within the range of 15°C to 35°C temperature had little influence. Most researchers, however, have found that within the temperature range of 10°C to 30°C the temperature effects can be simulated by the following expression:

$$k_n = k_{n_{20}} \theta^{T-20} \tag{3-49}$$

where $k_{n_{20}}$ = nitrification rate parameter at 20°C

θ = temperature correction factor

Since the oxidation rate of ammonia is typically much slower than the rate of nitrite oxidation to nitrate, the rate of the first reaction controls the overall reaction rate. Hence, values of θ for the ammonia oxidation reaction are the appropriate ones to use in the single stage formulation. Table 3-16 summarizes θ values found by different researchers for that reaction. The values are generally valid within a temperature range of 10°C to 30°C.

TABLE 3-16. TEMPERATURE CORRECTION FACTOR θ
FOR AMMONIA OXIDATION (McCARTY, UNPUBLISHED NOTES)

Reference	θ	ΔT for Doubling k_n
Stratton (1966)	1.0876	8.3°C
Knowles, *et al*. (1965)	1.0997	7.3°C
Garrett	1.0953	7.6°C
Buswell, *et al*. (1957)	1.0757	9.5°C
Wild, *et al*. (1971)	1.0548	13.0°C

Equation (3-49) indicates that nitrification rates monotonically increase with increasing temperature. Wild, et al. (1971) found this to be true for the temperature range of 5°C to 30°C. For temperatures above 30°C this may not be true, however, and there is clearly some maximum temperature above which the rate decreases rapidly. Outside of the range 5°C to 30°C Equation (3-49) should not be used. The optimum temperature for nitrification is generally accepted to be between 25°C to 28°C.

In surface waters, a stimulating effect of suspended particles on the nitrification rate has been reported by a number of workers (Kholdebarin and Oertli, 1977a). In their studies, Kholdebarin and Oertli collected water samples from the Whitewater River in the Coachella Valley in Southern California. Their findings indicated that although nitrifying organisms can function well in media lacking any measurable suspended solids, suspended particulates stimulated their activity. The authors felt that this effect was caused by the particles acting as sites for the proliferation of the nitrifying bacteria.

Many workers have reported that the bottoms of streams can also offer sites for the growth of nitrifying organisms (e.g., Matulewich and Finstein, 1975 and Blain (1969)). This is particularly true for rocky bottoms of shallow streams. Mills (1976) has documented evidence supporting this contention, as well as developing a mathematical model to simulate the process in natural streams.

Nitrification has also been shown to occur extensively in the top few centimeters of the sediments of the Rivers Trent and Tame in England. At least 80 percent of the observed ammonia nitrification in those rivers occurred there (Curtis, et al., 1975).

Bansal (1976) performed extensive analysis in relating k_n to different characteristics of natural streams by using dimensionless groups. The best correlations between predicted and observed values occurred when using the stream Reynolds and Froude numbers to predict k_n. These two dimensionless numbers depend primarily on temperature, depth, and velocity parameters which ordinarily are readily available or easily measurable. Bansal's work is somewhat controversial, however, and has been criticized by at least two workers (Gujer (1977) and Brosman (1977)). The reason for the criticisms is the fact that Bansal chose to ignore the biochemical aspects of nitrification and considered only hydraulic stream parameters.

3.6.3 Summary of Rate Values

Bansal (1976) has compiled k_n data for numerous rivers around the country. These values are shown in Table 3-17 which also contains k_d and k_2 data. Figure 3-8 shows Bansal's predictive formula for k_n and a plot of the line of best fit through the observed data points (data not plotted).

3.6.4 Measurement of Nitrification Rate

Depending on the kinetics formulation chosen to express nitrification, the number of kinetics parameters and rate coefficients to be evaluated will vary. Also, a variety of techniques have been used to measure these parameters. This discussion will be limited to a summary of methods used to measure k_n.

TABLE 3-17. NITRIFICATION RATE CONSTANTS (FROM BANSAL, 1976)

Discharge (cfs)	Cross-sectional Area (sq ft)	Top Width (ft)	Temperature °C	Reported k_d Base e day^{-1}	Reported k_2 Base e day^{-1}	k_n Reported
Grand River (Mich.)						
(295.0)	320.0	168.4	28.0	0.80	3.996	1.9
Truckee River (Nev.)						
(180.0)	150.0	89.82	27.8	0.09	5.625	2.4
(195.0)	150.0	89.82	27.8	0.49	5.902	2.4
(271.0)	150.0	89.82	27.8	1.30	7.190	2.4
Flint River (Mich.)						
134.0	210.0	100.0	28.0	0.76	2.786	2.0
174.0	200.0	76.92	28.0	0.95	2.487	0.1
174.0	400.0	153.85	28.0	0.95	1.641	0.1
204.0	290.0	170.59	28.0	0.95	3.971	2.5
204.0	400.0	210.5	28.0	0.95	2.801	2.5
Upper Mohawk River (N.Y.)						
143.0	2,400.0	200.0	20.0	0.23	0.063	0.25
143.0	2,400.0	200.0	20.0	0.23	0.063	0.25
147.0	2,400.0	200.0	20.0	0.23	0.064	0.25
305.0	2,400.0	200.0	20.0	0.23	0.099	0.25
176.0	120.0	48.0	20.0	0.40	3.875	0.30
185.0	120.0	48.0	20.0	0.40	3.993	0.30
318.0	120.0	48.0	20.0	0.40	5.526	0.30
195.0	120.0	40.0	20.0	0.40	3.193	0.30
205.0	120.0	40.0	20.0	0.40	3.290	0.30
353.0	120.0	40.0	20.0	0.40	4.558	0.30
301.0	200.0	64.5	20.0	0.40	2.911	0.30
340.0	200.0	64.5	20.0	0.40	3.132	0.30
729.0	200.0	64.5	20.0	0.40	4.950	0.30
331.0	200.0	57.1	20.0	0.40	2.599	0.30
374.0	200.0	57.1	20.0	0.40	2.796	0.30
801.0	200.0	57.1	20.0	0.40	4.416	0.30
392.0	700.0	189.2	20.0	0.40	1.256	0.30
451.0	700.0	189.2	20.0	0.40	1.366	0.30
1,018.0	700.0	189.2	20.0	0.40	2.227	0.30
392.0	1,500.0	375.0	20.0	0.40	0.713	0.30
451.0	1,500.0	375.0	20.0	0.40	0.775	0.30
1,018.0	1,500.0	375.0	20.0	0.40	1.264	0.30
557.0	650.0	100.0	20.0	0.23	0.737	0.25
656.0	650.0	100.0	20.0	0.23	0.813	0.25
1,525.0	650.0	100.0	20.0	0.23	1.348	0.25
1,088.0	900.0	120.0	20.0	0.23	0.741	0.25
1,272.0	900.0	120.0	20.0	0.23	0.814	0.25
3,655.0	900.0	120.0	20.0	0.23	1.534	0.25
1,108.0	3,800.0	422.2	20.0	0.23	0.245	0.25
1,286.0	3,800.0	422.2	20.0	0.23	0.267	0.25
3,727.0	3,800.0	422.2	20.0	0.23	0.506	0.25
1,128.0	700.0	70.0	20.0	0.23	0.589	0.25
1,311.0	700.0	70.0	20.0	0.23	0.644	0.25
3,799.0	700.0	70.0	20.0	0.23	1.220	0.25

(continued)

TABLE 3-17 (continued)

Discharge (cfs)	Cross-sectional Area (sq ft)	Top Width (ft)	Temperature °C	Reported k_d Base e day^{-1}	Reported k_2 Base e day^{-1}	k_n Reported
Middle Mohawk River (N.Y.)						
1,300.0	5,000.0	385.0	23.5	0.30	0.132	0.30
1,300.0	1,500.0	136.4	23.5	0.30	0.344	0.30
1,600.0	1,500.0	125.0	23.5	0.30	0.345	0.30
1,610.0	4,600.0	354.0	23.5	0.30	0.158	0.30
1,620.0	5,200.0	400.0	23.5	0.30	0.147	0.30
1,640.0	6,200.0	477.0	23.5	0.30	0.133	0.30
Lower Mohawk River (N.Y.)						
1,640.0	6,200.0	477.0	23.5	0.30	0.134	0.30
1,640.0	6,200.0	459.0	23.5	0.30	0.127	0.30
1,690.0	7,500.0	555.5	23.5	0.30	0.115	0.30
1,715.0	7,500.0	555.5	23.5	0.30	0.116	0.30
1,715.0	7,500.0	535.7	23.5	0.30	0.110	0.30
1,715.0	7,500.0	535.7	23.5	0.30	0.110	0.30
1,715.0	6,000.0	428.6	23.5	0.30	0.126	0.30
1,735.0	6,000.0	428.6	23.5	0.30	0.127	0.30
1,735.0	6,000.0	428.6	23.5	0.30	0.127	0.30
1,735.0	9,500.0	633.6	23.5	0.30	0.087	0.30
1,735.0	19,000.0	1,266.6	23.5	0.30	0.058	0.30
Barge Canal (parallel to upper Mohawk River)						
16.0	2,200.0	176.0	19.0	0.23	0.017	0.25
34.0	2,200.0	176.0	19.0	0.23	0.027	0.25
16.0	2,200.0	176.0	19.0	0.23	0.017	0.25
26.0	3,000.0	230.8	19.0	0.23	0.018	0.25
16.0	3,000.0	230.8	19.0	0.23	0.013	0.25
20.0	3,000.0	230.8	19.0	0.23	0.015	0.25
Ohio River-Markland Pool						
26,000.0	36,000.0	1,333.3	27.0	0.25	0.085	0.25
29,000.0	36,000.0	1,333.3	26.0	0.25	0.091	0.25
32,000.0	44,000.0	1,375.0	28.0	0.25	0.067	0.25
23,000.0	44,000.0	1,375.0	24.0	0.25	0.057	0.25
17,000.0	50,000.0	1,562.5	28.0	0.25	0.042	0.25
14,000.0	50,000.0	1,562.5	24.0	0.25	0.039	0.25
25,000.0	56,000.0	1,555.5	27.0	0.25	0.042	0.25
30,000.0	56,000.0	1,555.5	26.0	0.25	0.048	0.25
10,000.0	30,000.0	12,500.0	24.0	0.241*	1.624	0.25
20,000.0	35,000.0	14,000.0	16.0	0.25*	1.719	0.25
17,500.0	70,000.0	1,707.3	28.0	0.25	0.052	0.25
14,500.0	70,000.0	1,707.3	24.0	0.25	0.023	0.25
15,000.0	35,000.0	14,000.0	28.0	0.224*	2.291	0.25
Big Blue River (Nebr.)						
25.5	24.2	36.0	25.0	0.160	19.067	0.164
25.6	59.0	38.0	25.0	0.100	3.468	0.164

*Estimated values of k_d.

(continued)

TABLE 3-17 (continued)

Discharge (cfs)	Cross-sectional Area (sq ft)	Top Width (ft)	Temperature °C	Reported k_d Base e day^{-1}	Reported k_2 Base e day^{-1}	k_n Reported
Big Blue River (Nebr.)						
22.1	36.1	32.0	23.5	0.200	6.731	0.164
32.3	27.1	26.0	23.5	0.170	10.825	0.253
20.94	22.01	24.0	23.5	0.170	11.716	0.253
132.0	102.6	85.0	23.5	0.110	9.471	0.046
122.0	77.0	55.0	27.0	0.238*	8.552	0.051
152.0	85.2	50.0	26.0	0.239*	7.076	0.051
194.0	161.2	110.0	27.7	0.240*	6.774	0.051
210.0	96.4	79.0	28.0	0.237*	12.444	0.051
192.0	112.3	127.0	29.0	0.236*	16.740	0.108
295.0	190.0	126.0	29.0	0.243*	7.484	0.108
333.0	148.0	86.0	27.8	0.243*	7.840	0.032
Delaware River Estuary						
8,900.0	45,000.0	1,800.0	10.0	0.30**	0.051	0.085
8,900.0	145,000.0	7,000.0	10.0	0.30**	0.023	0.085
8,900.0	220,000.0	8,800.0	10.0	0.30**	0.020	0.085
5,600.0	45,000.0	1,800.0	21.0	0.30**	0.035	0.385
5,600.0	175,000.0	7,000.0	21.0	0.30**	0.015	0.385
5,600.0	220,000.0	8,800.0	21.0	0.30**	0.013	0.385
2,000.0	45,000.0	1,800.0	20.0	0.30**	0.019	0.325
2,000.0	175,000.0	7,000.0	20.0	0.30**	0.008	0.325
2,000.0	220,000.0	8,800.0	20.0	0.30**	0.007	0.325
3,000.0	45,000.0	1,800.0	26.0	0.30**	0.023	0.535
3,000.0	175,000.0	7,000.0	26.0	0.30**	0.010	0.535
3,000.0	220,000.0	8,800.0	26.0	0.30**	0.008	0.535

*Estimated values of k_d.

**These values of k_d are referenced to 20°C

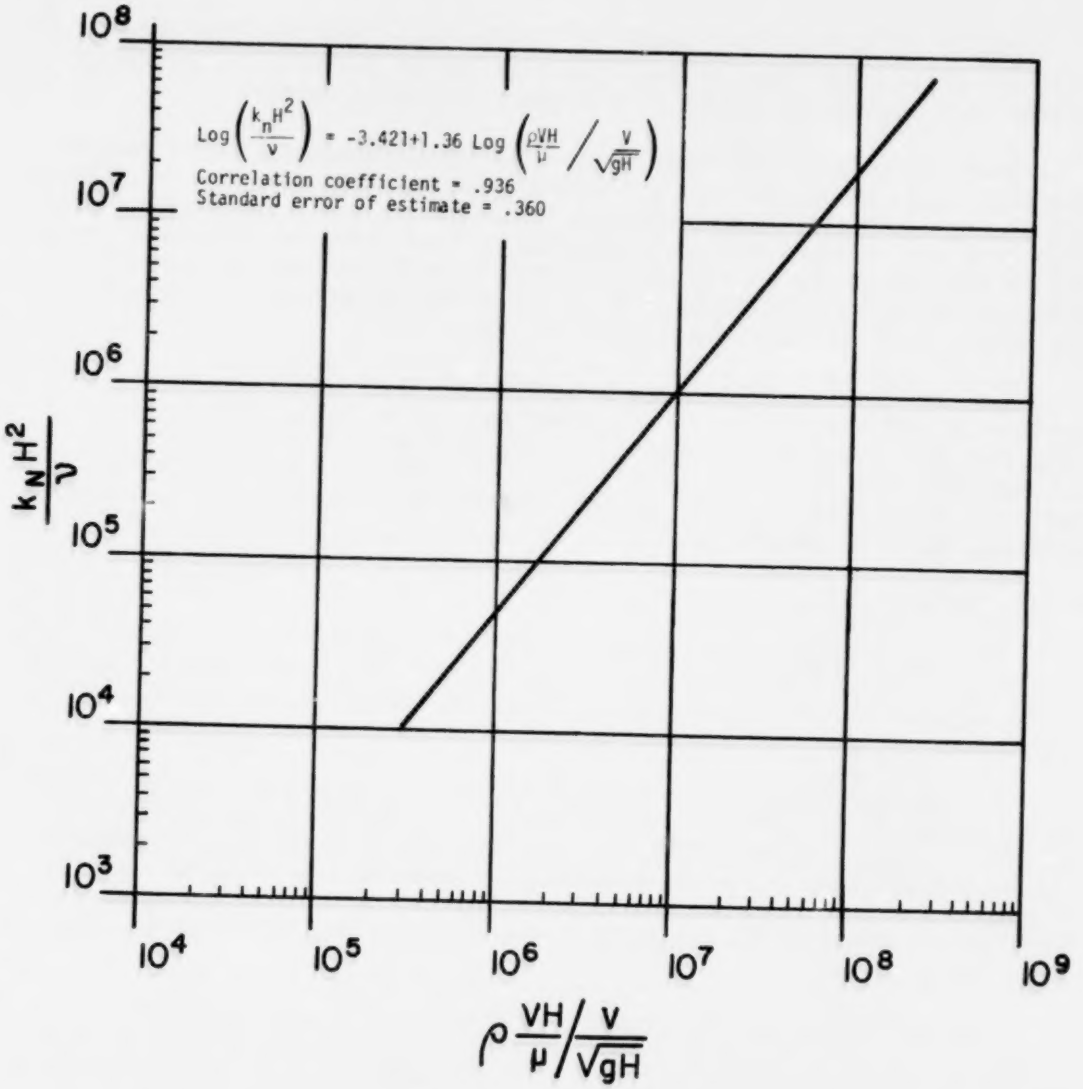

Figure 3-8. Nitrification parameter $k_n H^2/\nu$ versus the ratio of the Reynolds number $\rho VH/\mu$ and the Froude number (Bansal, 1976).

Courchaine (1968) has plotted nitrogenous BOD on a logarithmic scale, and determined the decay rate from the slope of the line. This is a procedure similar to that described in Section 3.5 for measuring carbonaceous BOD decay rates. Other mass-balance methods in that section, such as measuring k_d in a tidally influenced river, can be applied to determine k_n if the appropriate conditions are met. Nelder and Mead (1965) and Bard (1967) have also used data measured at two or more locations to estimate nitrification rates.

Thomann (1963) has determined k_n by plotting long-term BOD data on a semi-log plot. The slope of the line provides an estimate of the decay coefficient during the second (nitrogenous) stage of decay.

Thomann, et al. (1971) has taken a different approach to estimating nitrification rates. He used a finite-difference approximation to solve a set of simultaneous linear equations. The nitrification rates calculated from this set of equations were adjusted so that observed dissolved oxygen values throughout the stream were accurately reflected by the equations. Although Thomann simulated nitrification in two stages, his procedure is applicable to a single stage simulation approach.

Das and Cibulka (1976) have used the two-point method of Rhame (described in Nemerow (1974)) to determine k_n. To do this, they first inhibited nitrification using 2-chloro-6-(trichloromethyl) pyridine, as recommended in the U.S. EPA Training Manual (1974). The inhibited BOD curve was subtracted from the uninhibited curve resulting in a curve from which k_n could be determined.

3.6.5 Summary

The single stage representation of nitrification is certainly a simplification of the process, and some (Gujer (1977) and Brosman (1977)) would argue that it is an oversimplification. Nevertheless it is a widely used approach, and will probably continue to be so.

Methods for measuring k_n are varied, as discussed previously. There is no concensus as to which nitrogen forms are actually represented in in situ k_n observations. Some monitor only the disappearance of ammonia-nitrogen, and others, the disappearance of ammonia plus organic nitrogen. If the disappearance of ammonia-nitrogen is monitored, and no organic-nitrogen is present, the two methods will produce the same result; otherwise they will not.

The method most widely used to determine the stoichiometric equivalence between oxygen utilization and nitrification is to use the oxidation-reduction half reactions for nitrification, which produces a stoichiometric equivalence of 4.57. Using this approach yields a value which is a few percentage points higher than the true equivalence. However, because the actual value may change depending on environmental conditions, because a considerable effort would be required to improve upon the value, and because the 4.57 figure produces conservative results as far as dissolved oxygen mass-balance calculations are concerned, the higher figure can justifiably be used.

Any method for measuring k_n using in situ data based on an NBOD mass-balance equation should be studied to determine if the formulation assumptions are valid for the receiving water under consideration. Since the aquatic nitrogen cycle is complex (see Brezonik (1973)) somewhat obscure sources or sinks of NBOD may exist, and if significant, could affect the estimated k_n.

Laboratory measurements of k_n can produce results that differ significantly from what might be measured in situ. As discussed previously, benthic effects, pH, and suspended particle levels can affect nitrification rates, and all these factors cannot be simulated accurately in the laboratory. The methods previously discussed that deal with simply determining whether or not nitrification is occurring have taken the approach of evaluating k_n. Another method exists which, in a qualitative sense at least, can be used to determine whether or not nitrification occurs. This method involves determining directly whether a viable population of nitrifiers exists in situ. Relatively few researchers have done this, either as a supplement or as an integral part of their work in receiving waters. However, two cases should be mentioned. The first dealt with measuring Nitrosomonas and Nitrobacter in sediments of the Rivers Trent and Tame (Curtis, et al. (1975)), where large concentrations of these organisms were found. The second dealt with the evaluation of the same organisms in the Passaic River (Finstein, et al., 1977) where disagreement existed as to whether or not nitrification was occurring.

Low concentrations of nitrifiers (on the order of hundreds per milliliter) suggest that nitrification is unimportant, while high concentrations (on the order of millions per milliliter) indicate that nitrification is probably important.

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3.7 BENTHIC OXYGEN DEMAND

3.7.1 Introduction

Often, it is necessary to consider benthic oxygen demand when simulating dissolved oxygen in receiving waters, regardless of the water body type. Benthal deposits at any given location in an aquatic system are the result of the transportation and deposition of organic material. The material may be from an outside source (allochthonous material), or it may have local origins (autochthonous material). In either case such organic matter can exert a high oxygen demand under some circumstances.

Many investigators (e.g., Martin and Bella, 1971) have shown that the rate of oxygen demand is influenced by two different phenomena. The first is the rate at which oxygen diffuses into the bottom sediments and is then consumed. The second is essentially the rate at which reduced organic substances are conveyed into the water column, and are then oxidized. Traditional measurement techniques, whether they be performed *in situ* or in the laboratory, do not differentiate between the two processes but measure, either directly or indirectly, the gross oxygen uptake. Hence, in modeling dissolved oxygen, a single term in the dissolved oxygen mass balance formulation is normally used for both processes. If the two phenomena are modeled separately, then an additional BOD source is included in the BOD mass balance to account for the organic material being added to the water column from the benthos. Concurrently, a lesser benthic demand is used in the dissolved oxygen mass balance. Ogunrombi and Dobbins (1970) investigated these two phenomena, and developed expressions for the BOD and DO mass balances. In the experiments they performed (using a synthetic mixture approximating heavily polluted stream water), they found that the BOD which diffused back into the overlying water was 28 percent as large as the oxygen demand caused by oxygen diffusing into the benthic deposits.

In the discussion that follows, the gross benthic oxygen demand will be treated as a single term.

3.7.2 Factors Affecting Benthic Oxygen Demand

Values of benthal oxygen uptake can vary considerably as will be shown in Section 3.7.3. Hunter, et al. (1973), and others, have undertaken studies to determine exactly what characteristics of the benthic deposits were significant in affecting the uptake rates. Hunter, et al. first looked at the chemical constituents comprising the benthic material. He examined percent moisture, percent volatile, kjeldahl nitrogen, COD, BOD_5, BOD_{20}, TOC and hexane-benzene extractables. Hunter then used multiple regression analyses to find out how these constituents correlated with observed benthic oxygen demands. The one constituent that explained most of the variance of uptake rates was COD. However, it explained only 37% of the variance, and the relationship was found to be not significant at the 95% confidence level.

Hunter, et al. then continued the analyses by examining the influence of biological constituents, in particular the benthic macroinvertebrate population. They found strong correlations between benthic demand rate and the presence of tubificial worms, although the respiration of the worms comprised only a small fraction of the benthic demand. Hunter, et al. hypothesized several possible mechanisms for the worms' influence on oxygen demand. These included: 1) an increase in the depth to which oxygen diffuses in the deposit, 2) an increase in the effective surface area over which uptake can occur, and 3) the transport of organic substances to the benthic surface by the worms.

The findings of Hunter, et al. concerning the importance of macroinvertebrates are supported by the earlier work of Rolley and Owens (1967). Like Hunter, et al., Edeberg and Hofsten (1973) also found that no simple correlations existed between the organic content in the sediment and the oxygen uptake rate.

The effects of sediment depth on oxygen consumption have been studied. For sewage sludge, Baity (1938) developed the following equation:

$$S_B = a\ D^{0.485} \qquad (3\text{-}50)$$

where D = depth of sediment, cm

a = an empirical constant (found to be 2.7 at 22°C)

S_B = benthic uptake rate of oxygen, gm/m^2-day

The maximum depth that was used in Equation (3-50) was 20 cm. Not all researchers have agreed with the equation and its constants, however. Fillos and Molof (1972) found oxygen uptake to be independent of sediment depths greater than 10 cm. Stein and Denison (1967) found no evidence of increased oxygen uptake at increasing sediment depths, while Davidson and Hanes (1968) found that deeper deposits of freshly deposited cellulosic material exerted a significantly greater oxygen uptake than shallower deposits. Here, however, once consolidation of the bottom deposit was essentially complete, the oxygen uptake rate became independent of depth.

The benthic oxygen consumption rate also has been hypothesized to depend on the dissolved oxygen concentration in the overlying waters. Many researchers (e.g., Edwards and Rolley, 1965; McDonnell and Hall, 1969) have hypothesized the relationship to be:

$$S_B = a\ C^b \tag{3-51}$$

where C = dissolved oxygen concentration

a,b = empirically determined constants

In the McDonnell and Hall (1969) study b was found to be 0.30 and a to vary from 0.09 to 0.16. The dissolved oxygen concentrations ranged from 0.5 mg/l to 6.0 mg/l.

Lombardo (1972) also computes the benthic oxygen demand as a function of overlying dissolved oxygen concentration:

$$S_B = a\left(1 - e^{-1.22C}\right) \tag{3-52}$$

where a = constant depending on nature of deposits (0.96 to 8.52 for S_B in gm/m^2-day)

That the overlying dissolved oxygen concentration is important in influencing the benthal demand remains in dispute. Martin and Bella (1971) showed that benthal oxygen consumption appears independent of the oxygen concentration in the water for dissolved oxygen values above 2 mg/l. They reasoned that the benthal oxygen uptake was primarily caused by release of oxygen-demanding substances, and not the diffusion of oxygen into the benthos.

Martin and Bella (1971) have also investigated the effects of overlying water mixing rates on the benthic oxygen demand. Samples were collected from the Yaquina Estuary near Newport, Oregon. The mixing speed in the apparatus used for testing was adjusted so that the suspended solids in the apparatus compared with the suspended solids measurements taken in the estuary. Results showed the average unmixed oxygen uptake to be 1.9 gm/m^2-day, while the uptake rate under mixed conditions was 80 percent higher.

Perhaps the best documented and most agreed upon factor affecting benthic oxygen demand is temperature. Many investigators who incorporate benthic demand into their models prefer to estimate the benthic demand at a reference temperature (usually 20°C) and then incorporate a temperature correction factor for other temperatures. The relationship can be expressed as:

$$S_B = S_{B_{20}} \theta^{T-20} \tag{3-53}$$

where the reference temperature is 20°C. Many different values of θ have been determined. These are summarized in Table 3-18.

TABLE 3-18. THE EFFECT OF TEMPERATURE ON BENTHIC OXYGEN UPTAKE

Researcher	Range (°C)	Temperature Coefficient, θ	$\frac{S_{B_{(T+10)}}}{S_{B_T}}$
Edeberg and Hofsten (1973)	5-15	1.130	3.4
Edeberg and Hofsten (1973)	10-20	1.080	2.1
Edeberg and Hofsten (1973)	15-25	1.040	1.5
Edwards and Rolley (1965)	10-20	1.077	2.1
Karlgren (1968)	2-22	1.090	2.4
McDonnell and Hall (1969)	5-25	1.067	1.9
Pamatmat (1971)	5-10	1.088	2.7
Pamatmat (1971)	5-15	1.041	1.5
Thomann (1972)	10-30	1.065	1.9

The last column in the table indicates how a 10°C temperature increase affects the uptake rate. A temperature coefficient of 1.0718 results in a doubling of the uptake rate for a 10°C increase. Many researchers have found that the temperature coefficient decreases somewhat with increasing temperature (see Table 3-18).

3.7.3 Values of Benthic Oxygen Uptake

Table 3-19 summarizes values obtained by Hunter, et al. (1973) from which they tried to develop correlations between chemical characteristics of the deposits and benthic oxygen demand. They also collected additional samples within the Passaic River to investigate the relationship of benthic demand to invertebrate population. These results are shown in Table 3-20. The distance measurements in the table are with respect to Pine Brook, where a heavy waste load enters the river. Below that point there are no known point sources. Thus, the river in the region under investigation represents a polluted zone followed by a zone of gradual improvement. All of Hunter's measurements were carried out *in situ* using a benthic respirometer.

TABLE 3-19. SOURCE AND GENERAL CHARACTERISTICS OF BENTHAL DEPOSITS (HUNTER, ET AL. 1973)

#	Source (River)	Benthal Oxygen Demand $g/m^2/d$	Moisture %	Volatile Solids %	TOC mg/g	COD mg/g	BOD_5 mg/g	Kjel.N mg/g
1	Passaic	10.141	52.2	12.4	297	2245	75	3.8
2	Passaic	12.76	42.7	10.8	326	4064	82	3.2
3	Passaic	2.423	51.5	14.8	278	3272	190	3.3
4	Passaic	2.284	52.7	12.0	209	2639	80	3.5
5	Passaic	1.981	52.4	12.6	584	2640	70	4.4
6	Passaic	1.888	48.1	11.4	750	2563	125	3.6
7	Passaic	1.726	49.2	11.2	311	2482	162	4.0
8	Elizabeth	9.81	38.2	11.7	289	3724	190	1.6
9	Millstone	2.012	40.8	7.4	280	1281	23	0.6
10	Mile Run	1.083	24.3	5.6	144	713	5	1.1

TABLE 3-20. RELATIONSHIP BETWEEN BENTHAL OXYGEN DEMAND AND TUBIFEX WORM POPULATION (HUNTER, *ET AL*., 1973)

Station	Distance ft.	Benthal Oxygen Demand, grams/ meter^2/day	Tubifex Worms Numbers/ft^2	Oxygen Demand mg/worm/day
I	- 100	11.45	26,400	0.035
III	+ 1,800	6.42	11,160	0.041
IV	+15,000	2.42	3,800	0.022
V	+30,000	1.89	3,000	0.012
VI	+50,000	1.73	400	0.049

Edeberg and Hofsten (1973) conducted both *in situ* and laboratory experiments for receiving water bodies in Sweden. Their results are shown in Table 3-21. The *in situ* values were generally found to be considerably higher than the laboratory values. The authors felt these differences were caused by the disruption of sediment structure and biological conditions during sampling, and the difference between natural and contrived laboratory conditions.

Rolley and Owens (1967) investigated the sediments from 74 sites in 12 river systems in southern England. The rates of oxygen consumption varied from 0.144 gm/m^2-day to 9.84 gm/m^2-day. A summary of their findings is presented in Table 3-22. No significant difference was found between rates of oxygen consumption in winter and summer in any of the first four groups. The fifth group (Group E) was not analyzed because of the heterogeneous nature of the sites. Also, it was found the demands from Groups A and B were similar for any given parameter and equal to approximately half the values found in Groups C and D. It should be noted that the volumetric discharge from the activated sludge treatment plants was considerably higher than that from the trickling filter plants.

Thomann (1972) has also compiled data from various sources and this information is presented in Table 3-23.

3.7.4 Measurement Techniques

There are two major categories of techniques for measuring benthic oxygen demand: *in situ* techniques and laboratory analysis techniques.

TABLE 3-21. OXYGEN CONSUMPTION OF SEDIMENTS IN THE LABORATORY AND IN SITU (FROM EDEBERG AND HOFSTEN, 1973)

Site	Date	Org. Matter (Dry Weight)	Temp. (°C)	Oxygen Consumption in Laboratory ($g\ O_2\ m^{-2}\ d^{-1}$)	Temp. (°C)	Oxygen Consumption in situ ($g\ O_2\ m^{-2}\ d^{-1}$)
The Baltic (Salinity 4-6.7 ‰)						
Askö 1	7/15/71	12.8	-	-	15	2.5
Askö 1	9/ 1/71	12.8	-	-	15	1.1
Askö 2	8/31/71	7.9	-	-	16	1.2
Edeboviken 1*	6/29/72	17.7	10	0.71	13	3.0
Edeboviken 2*	6/29/72	11.4	10	0.40	15	0.92
Karlholm 1[†]	7/28/71	19.0	-	-	15	0.93
Karlholm 2[†]	7/29/71	60.5	-	-	17	1.3
Karlholm 3	7/30/71	2.6	-	-	17	1.7
Lakes						
Ekoln**	8/18/71	0.6	13	0.58-1.2	18	2.6
Erken 1	3/22/72	-	10	0.32-0.36	4	0.43
Erken 2	7/ 9/71	1.3	-	-	14	0.50
Norrviken 1**	5/ 4/72	40.	10	1.1	5	1.8
Norrviken 2**	5/ 4/72	30.	10	1.5	7	2.4
Ramsen	8/26/71	12.2	10	0.21-1.08	17	2.3
Running Waters						
Arbogaan 1 Venaviken	3/ 8/72	-	5	0.26-1.2	2	1.44
	10/ 7/71	10.3	-	-	10	0.68
Arbogaan 2 Sjomosjon	3/ 8/72	11.	10	0.31-0.61	0	0.31
Arbogaan 3 Jaders Bruk	10/ 8/71	8.5	-	-	9	0.84
	3/ 8/72	-	5	0.42-0.63	2	1.4

* Sediment contains fibrous matter from a papermill where sulphite and groundwood pulp is produced.

[†] Sediment contains fibrous matter from a hard board mill.

** Eutrophic lake with newly deposited algae.

TABLE 3-22. RATES OF OXYGEN CONSUMPTION AND CHEMICAL PROPERTIES OF MUD DEPOSITS SAMPLED FROM VARIOUS SITES (AFTER ROLLEY AND OWENS, 1967)

			BELOW EFFLUENTS			
		Group A** (12)	Group B (21)	Group C (10)	Group D (5)	Group E (21-23)
Oxygen consumption (g/m^2 per day at 15°C at oxygen level of 7 mg/l)	Winter	1.2	1.2	2.4	2.4	1.68
	Summer	1.44	1.44	3.36	2.4	1.2
Permanganate value ($g\ O_2$/100 g* in 4 hr. at 27°C)		5.4±2.6	5.7±2.7	7.6±3.7	10.7±2.9	6.2
Humic acid (g/100 g)		2.4±1.4	2.5±1.3	3.0±2.1	4.7±2.1	3.2
Loss on ignition (g/100 g)		10.7±4.3	10.7±4.4	15.4±7.8	20.9±7.7	13.1
Organic carbon (C) (g/100 g)		6.1±3.6	5.7±2.7	7.5±4.8	11.8±3.7	6.3
Kjeldanl nitrogen (N) (g/100 g)		0.5±0.2	0.6±0.3	0.8±0.5	1.2±0.6	0.5
C/N ratio		10.3±3.9	10.2±3.2	9.3±2.2	10.9±2.9	9.8
Humic acid/C ratio		0.4±0.2	0.5±0.2	0.5±0.2	0.4±0.2	0.5

* All chemical properties are for 100 g dried mud.

** Group definitions:

- (A) Sites above effluent outfalls that are free from polluting influences (12 sites).
- (B) Sites affected by effluents from percolating-filter plants operating to nominal standards of 30 mg/l suspended solids and 20 mg/l biochemical oxygen demand (BOD) (21 sites).
- (C) Sites affected by effluents from percolating-filter plants operating to nominal standards of 50 mg/l suspended solids and 30 mg/l BOD (10 sites).
- (D) Sites affected by effluents from activated-sludge plants (5 sites).
- (E) Sites not suitable for inclusion in the above groups (23 sites). These include sites receiving effluents from mixed treatment works and also sites where the upstream flow or discharge pattern was complex.

TABLE 3-23. AVERAGE VALUES OF OXYGEN UPTAKE RATES OF RIVER BOTTOMS (AFTER THOMANN, 1972)

Bottom Type and Location	Uptake (gms O_2/m^2-day) @ 20°C Range	Approximate Average
Sphaerotilus - (10 gm dry wt/m^2)	-	7
Municipal Sewage Sludge-Outfall Vicinity	2-10.0	4
Municipal Sewage Sludge-"Aged" Downstream of Outfall	1-2	1.5
Cellulosic Fiber Sludge	4-10	7
Estuarine mud	1-2	1.5
Sandy bottom	0.2-1.0	0.5
Mineral soils	0.05-0.1	0.07

Hunter, et al. (1973) used a benthal respirometer of the type described by Stein and Denison (1967) to make in situ measurements. The respirometer is an opaque chamber (to prevent photosynthesis) that is lowered to the stream bottom where its open face is in contact with the mud surface. The oxygen level of the water in the chamber is determined for as long a period as possible, while not allowing the dissolved oxygen to fall below 0.5 mg/l. The oxygen consumed is then calculated from the difference between the initial and final DO concentrations, and corrected using a BOD determination of the river water at the same temperature over the same area. Edeberg and Hofsten (1973) also used the method of Stein and Denison, but with some modifications.

The kajak bottom sampler (Edmonson and Winberg, 1971) has been used to obtain sediment cores for laboratory benthic oxygen demand analysis. Edeberg and Hofsten (1973) modified this technique slightly. They used a plexiglas sediment sampling tube which was 500 mm in length and 70 mm in diameter. The laboratory experiments were carried out directly in these tubes in the dark, and at constant temperature. A magnetic stirrer was used to keep the water above the sediment homogeneous, and an oxygen electrode was used for oxygen measurements.

Martin and Bella (1971) used an apparatus that mixed the mud surface with the overlying water. Mixing blades were immersed in each sampling tube, the height above the mud and rotation rate being adjustable. Samples were collected in water below the low tide mark so that no sample was taken in an area normally exposed at low tide. After the tubes were pushed onto the mud and the samples collected, each tube was reaerated to saturation and a 4-inch layer of mineral oil was floated on the surface to prevent reaeration. McDonnell and Hall (1969) used similar procedures in their work at Spring Creek, a highly eutrophic stream in central Pennsylvania. Other laboratory techniques have been described in Hanes and Irvine (1966), Edwards and Rolley (1965), and Knowles, et al. (1962).

3.7.5 Summary

The numerical values of benthic oxygen demand that have been presented here vary considerably, ranging from approximately 0.1 to 10.0 gm/m^2-day. There is no universal agreement on the factors causing this variation. Hence there is no one expression which has achieved general acceptance for computing S_B in receiving waters.

In contrast, the temperature correction factor has received more universal acceptance. Substantial variation in values for this factor, though, has also been observed by numerous researchers. Several researchers recommend a temperature correction factor, θ, such that the benthic uptake rate is doubled for every 10°C (which would correspond to $\theta = 1.0718$).

If it is undesirable to use a predictive formula to calculate S_B, there remain the alternatives of either using tabulated values, or directly measuring the uptake rate. For systems such as small lakes, where the uptake rate can be assumed spatially constant, only one measurement or estimate need be made. However for systems with large spatial variations, there is evidence (e.g., Hunter, et al. (1973) and Rolley and Owens (1967)) that the benthic uptake can significantly change over distance within the water body. Accordingly, one measurement or estimate may not be sufficient to accurately characterize benthic uptake.

If direct measurement is not possible or is impractical, the selection of literature values should be guided by the following considerations as a minimum:

- similarity of water bodies
- temperature of measurement and temperature correction needed to correct rate to water body being modeled
- location with respect to discharges, and the source rate and uniformity of benthic material

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3.8 COLIFORM BACTERIA

3.8.1 Introduction

The abundance of coliforms in natural waters has traditionally been used as an indicator of pathogen contamination. In the past, it was generally believed that coliform bacteria are not as sensitive to environmental stresses as organisms more commonly considered as pathogenic*. Accordingly, it was felt that coliforms are more persistent in natural waters and are, therefore, a "safe," and conservative index of pathogen contamination. Lombardo (1972) reports, however, that this may not be true under all circumstances. Data presented by Gallagher and Sino (in Lombardo, 1972) show that the numbers of the pathogen *Salmonella typhimurium* decline more slowly than numbers of coliforms, and it is clear that there is no reason to assume that coliform die-off rates are lower than those of all other pathogenic forms.

In discussing the impact of light on die-off rates of coliforms, Chamberlin and Mitchell (in press) have noted that fecal streptococci also do not necessarily die off at the same rate as do coliforms. As a result of reported findings such as these, the widespread practice of using numbers of coliform bacteria as an indicator of pathogen contamination is now subject to question.

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*It should be noted first that coliforms themselves can be pathogenic under certain conditions as in the mammalian urinary tract, and second, that the pathogenic organisms once believed more susceptible do not include most viruses, about which little is known regarding persistence.

3.8.2 Composition and Assay

The coliform group consists of fecal and non-fecal components. The fecal component is comprised of the enteric Escherichia group, while the non-fecal component represents the genus Aerobacter commonly found in soils and on leaves and grain.

The usual method of assaying for coliforms using the multiple tube fermentation technique does not differentiate between coliforms of fecal and non-fecal origin. To differentiate between Escherichia and Aerobacter, other, more time-consuming procedures are required, such as incubation at elevated temperature, and inoculation onto selective media such as eosin-methylene blue (EMB) agar. High temperatures inhibit non-fecal coliforms, and fecal coliforms respond in characteristic ways on the selective media, thus permitting assay of the fecal component of total coliforms.

The non-fecal coliform component is of limited sanitary significance and is capable of regrowth in nutrient-rich waters. Fecal coliforms, usually representing about 15 percent of the total (Lombardo, 1972) generally require conditions different from those in unpolluted or moderately polluted streams, and whether regrowth actually occurs in natural waters is still in doubt.

The fecal streptococcus is another measure of the bacteriological quality of a water body. The presence of "fecal streps" in streams is generally an indication of fecal contamination. The ratio of fecal coliforms to fecal streptococci can be used as an indication of the source of fecal pollution. According to Goldreich and Kenner as reported by Lombardo (1972), human feces would have a ratio not greater than 0.7. Clearly, however, this concept would only be useful where fecal contamination is fresh or where the relative loss of each species is known so that different die-off rates can be accounted for.

3.8.3 Modeling Coliforms

Modeling of coliforms is done for one main reason--establishing the level of fecal and/or soil pollution and potential pathogen contamination. The usual approach is simply to simulate die-off and to estimate coliform levels as a function of initial loading and the die-off rate which, in turn, is a function of time or distance of travel from the source.

3.8.3.1 Factors Affecting Die-Off Rates

Upon discharge to a water body, environmental conditions determine the extent to which coliform regrowth and death occur. Fecal coliforms and streptococci are occasionally observed to increase in numbers, although this may be due to disaggregation of clumps of organisms. Non-fecal organisms may, in fact, increase in numbers in natural waters where conditions are adequate (Lombardo, 1972; Mitchell and Chamberlin, in press).

Several physical factors can affect the coliform population in natural waters, resulting in an apparent increase or decrease in the coliform die-off rate. These factors include:

- Photo-oxidation
- Adsorption
- Flocculation
- Coagulation
- Sedimentation

Physicochemical factors include:

- Osmotic effects
- pH
- Chemical toxicity
- Redox potential

Biochemical and biological factors include:

- Nutrient levels
- Presence of organic substances
- Predators
- Bacteriophages (viruses)
- Algae
- Presence of fecal matter

3.8.3.1.1 Physical Factors

Chamberlin and Mitchell (in press) have noted that although much data has been collected on coliform die-off rates, mechanisms mediating the rates have historically been poorly understood. According to Chamberlin and Mitchell, however, light is one of the important factors. They observe that it is difficult to show statistically significant relationships between coliform die-off rates and factors usually hypothesized as influencing those rates. In contrast, significant relationships between light intensity and coliform die-off rates can be demonstrated. Chamberlin and Mitchell (in press) have shown that field data statistically support the photo-oxidation model (to be discussed), and data presented by Wallis, *et al*. (1977) also appear to implicate incident light. Chamberlin and Mitchell (in press) have elaborated upon possible mechanisms by which light may increase coliform die-off rates. They point out that although in many cases of light induced mortality, one or more photosensitizing substances are involved, visible and near ultraviolet light can kill *E. coli* in the absence of exogenous photosensitizers.

One suggested mechanism is that light quanta drive some exogenous or endogenous chromophore to an electronically excited state. The chromophore, in the process of returning to the ground state, transfers its absorbed light energy to another substance to form superoxides ($O_2\cdot$), which in turn cause damage to cellular components. Alternatively, the activated chromophore may cause damage directly, without the agency of a superoxygenated intermediate.

Several substances present in bacterial cells are effective photosensitizers. These include tryptophan (an amino acid) and porphyrins. Also, the photosensitizing substance may originate outside the coliform cell--for example, as a result of algal biosynthesis.

Adsorption, coagulation, and flocculation may affect coliform die-off rates, although few quantitative data are available. Adsorption refers to the attachment of coliform organisms to suspended particles. Coagulation refers to the coalescence of bacteria into clumps, and flocculation refers to the formation of soft, loose aggregates incorporating much water.

According to Mitchell and Chamberlin (in press), early investigations by several workers have demonstrated that clays tend to adsorb coliforms more than do silts or sands. This is, of course, commonly the case with sorbed substances. As Mitchell and Chamberlin point out, the nature and stability of coliform aggregates incorporating other particulate matter depends to a very large extent upon the physicochemical nature of the particles.

Sedimentation involves the settling out of bacterial particles and aggregates. The rate of die-off may be materially influenced by aggregation and sedimentation, but the magnitude and direction of the change in rate is not well understood. The mechanism of apparent die off due to sedimentation is actually simple removal of cells from the water column--that is, transfer of matter from one physical compartment (the water column) to another (the benthos). Accordingly, modeling coliform die off in the water column may give misleading results particularly where shellfish are harvested for human consumption. Reduction in coliform levels in the water column may simply mean increased numbers in the benthos.

3.8.3.1.2 Physicochemical Factors

Mitchell and Chamberlin (in press) report that physicochemical factors may have significant effects on die-off rates. Survival rates of *E. coli*, for example, are inversely proportional to salinity both in natural seawater (due to osmotic and other effects) and in artificial salt solutions. In general, *E. coli* have been found to survive longer in lower pH salt solutions ($pH < 8$) than under alkaline conditions.

Heavy metal toxicity toward microorganisms has been known since the late nineteenth century. A great number of studies have been done on the "oligodynamic action" of silver and copper salts. According to Mitchell and Chamberlin (in press), heavy metals have been implicated as important mediators of *E. coli* die-off rates, and the heavy metal effects may be reduced by addition of chelating agents. Redox potential, through its effect on heavy metals solubilities, also affects die-off rates. In addition to this, redox may influence die-off rates in other ways, although data on this are not extensive.

3.8.3.1.3 Biochemical and Biological Factors

Nutrient concentrations may be important in determining die-off rates under some conditions. In many nutrient studies, the apparent impact of nutrient addition to the coliform culture is due to chelation of heavy metal ions (Mitchell and Chamberlin, in press). Thus the apparent decrease in die-off rate in many cases may not be due to the additional nutrient, but instead, to reduced toxicity of the culture medium. Mitchell and Chamberlin (in press) cite the work of Jones (1964) who found that E. coli would not grow at 37°C in either filter-sterilized natural or synthetic seawater supplemented with glucose, ammonium chloride, and potassium phosphate. Inhibition could be reversed by autoclaving, by addition of very small amounts of organic matter, or by addition of metal chelating or complexing agents. Jones demonstrated that low levels of toxic metals would produce the inhibitory effect, and concluded that the apparent influence on die-off rates was due to naturally occurring trace heavy metals in solution. Furthermore, as Mitchell and Chamberlin (in press) note, other researchers have obtained experimental results implicating heavy metals, and their chelation upon addition of nutrients, in apparent changes in die-off rates.

In some situations, it appears that nutrient levels influence die-off rates in ways unrelated to toxic metals availability. Savage and Hanes (1971), for example, have reported growth-limiting effects of available BOD. Finally, it is possible that the level of nutrients affects coliform predators, thereby influencing rates of grazing on coliforms. Mitchell and Chamberlin (in press) report that predators in natural waters may be significant in reducing coliform populations. They cite three groups of microorganisms which may be important in seawater. These are cell wall-lytic marine bacteria, certain marine amoebae, and marine bacterial parasites similar to Bdellovibrio bacteriovorus. Experiments performed by a number of researchers have implicated predators in die-off of coliforms in both fresh and seawater. Bacteriophages, on the other hand, are apparently of minor importance, despite their demonstrated presence in sea water. The relative insignificance of phages, according to Mitchell and Chamberlin (in press), stems from their ineffectiveness in killing E. coli where the bacterial cells are not actively growing and multiplying, and the rapid inactivation of the phages by seawater.

Some forms of phytoplankton produce antibacterial agents which are excreted into the water column. These substances are heat-labile macromolecules, and according to Mitchell and Chamberlin (in press), at least one, a chlorophyllide, is active only if the system is illuminated. The fact that at least one antibacterial agent is activated by light suggests that algae may play a mediating role in the effect of light on die-off rates.

Other mechanisms of algal anti-coliform activity have been suggested. One is that during algal blooms, other organisms which prey on both algae and coliforms may also increase in numbers.

Table 3-24 is a summary of factors influencing coliform die-off rates.

TABLE 3-24. FACTORS AFFECTING COLIFORM DIE-OFF RATE
(ABSTRACTED FROM MITCHELL AND CHAMBERLIN, IN PRESS)

Factor	Effects
Sedimentation	Important with regard to water column coliform levels, particularly where untreated or primary sewage effluent is involved, and under low vertical mixing conditions. May adversely affect shellfish beds by depositing coliforms and fecal matter into benthos.
Adsorption, Coagulation, Flocculation	Inconclusive.
Solar Radiation	Important; high levels may cause more than 10-fold increase in die-off rate over corresponding rate in the dark in seawater. Rates also materially increased in freshwater.
Nutrient Deficiencies	Appears to accelerate die-off. Numerous studies have indicated that increasing nutrient levels of seawater decrease die-off rates. Some studies have shown that substantial nutrient additions appear to stimulate growth but actually may simply cause clump disaggregation.
Predation	Several species of organisms (bacteria, amoebae) have been shown to attack and destroy E. coli. Importance of predation is well established, but general guidelines for estimating extent of predation are difficult to provide without field data.
Bacteriophages	Apparently not important.

(continued)

TABLE 3-24. (Continued)

Factor	Effects
Algae	Bactericidal substances are known to be produced by planktonic algae. Substances may be photoactivators, mediating the influence of light on coliform die-off. This might account for variability of data in studies of light-induced die-off rates. Another hypothesis is that algal predators with blooms concomitant with algal blooms may produce substances toxic to *E. coli* or may prey upon them.
Bacterial Toxins	Antibiotic substances produced by indigenous bacteria are not believed important in coliform die-off.
Physicochemical Factors	Apparently, pH, heavy metals content, and the presence of organic chelating substances mediate coliform die-off rates. Importance of each, however, is poorly understood at present.

3.8.3.2 Modeling Formulations

Traditionally, coliform modeling has only taken into account die-off, and a simple first-order kinetics approach has been used (Baca and Arnett, 1976; Tetra Tech, 1975; Tetra Tech, 1976a; U.S. Army Corps of Engineers, 1974; Chen and Orlob, 1975; Lombardo, 1973; Lombardo, 1972; Anderson, *et al.*, 1976; Huber, *et al.*, 1972; Hydroscience, 1971; Chen and Wells, 1975; Tetra Tech, 1976b):

$$\frac{dC}{dt} = -kC \qquad (3\text{-}54)$$

or

$$C_t = C_o e^{-kt} \qquad (3\text{-}55)$$

where C = coliform concentration, mg/l

C_o = initial coliform concentration, mg/l

C_t = coliform concentration at time t, mg/l

k = die-off rate constant, day^{-1}

A summarized listing of values for k is presented in Table 3-25. The data summarize 28 studies of rates measured *in situ*. Table 3-26 shows values for k from a number of modeling studies. The median rate for the *in situ* studies is .04 hr^{-1} with 60 percent of the values less than .05 hr^{-1} and 90 percent less than .11 hr^{-1}.

A number of researchers have determined values for the half saturation constant (K_S) for *E. coli* growth, using the Monod expression:

$$\mu = \frac{\mu_M s}{K_s + s} \qquad (3\text{-}56)$$

where μ = growth rate at nutrient concentration s, day^{-1}

s = concentration of growth limiting nutrient, mg/l

μ_M = maximum growth rate, day^{-1}

K_s = half saturation constant producing the half maximal value of μ, mg/l

Table 3-27 shows some reported values for K_S.

TABLE 3-25. COLIFORM BACTERIA FRESHWATER DIE-OFF RATES MEASURED IN SITU (AFTER MITCHELL AND CHAMBERLIN, IN PRESS)

System	T (°C)	k(hr^{-1}, Base e)	Reference
Ohio River	Summer (20°C)	0.049	Frost and Streeter (1924)
	Winter (5°C)	0.045	
Upper Illinois River	June-Sept.	0.085	Hoskins, *et al*. (1927)
	Oct. and May	0.105	
	Dec.-Mar.	0.024	
	Apr. and Nov.	0.043	
Lower Illinois River	June-Sept.	0.085	Hoskins, *et al*. (1927)
	Oct. and May	0.037	
	Dec.-Mar.	0.026	
	Apr. and Nov.	0.029	
"Shallow Turbulent Stream"		0.63	Kittrell and Kochtitzky (1947)
Missouri River	Winter	0.020	Kittrell and Furfari (1963)
Tennessee R. (Knoxville)	Summer	0.043	Kittrell and Furfari (1963)
Tennessee R. (Chattanooga)	Summer	0.055	Kittrell and Furfari (1963)
Sacramento River	Summer	0.072	Kittrell and Furfari (1963)
Cumberland River	Summer	0.23	Kittrell and Furfari (1963)
Glatt River		1.1	Wasser, *et al*. (1934)
Groundwater Stream	10°	0.021	Wuhrmann (1972)
Leaf River (Miss.)		0.017	Mahloch (1974)
Wastewater Lagoon	7.9-25.5	0.00833-0.029	Klock (1971)
Maturation Ponds	-	0.083	Marais (1974)
	19°C	0.07	
Oxidation Ponds	"T"	$k = 0.108 \cdot (1.19)^{T-20}$	Marais (1974)

TABLE 3-26. VALUES FOR COLIFORM SPECIFIC DIE-OFF RATES USED IN SEVERAL MODELING STUDIES

System	k @20°C, hr^{-1}	Reference
North Fork Kings River, California	.042	Tetra Tech (1976a)
Various Streams	.0004-.146	Baca and Arnett (1976)
Lake Ontario	.02-.083	U.S. Army Corps of Engineers (1974)
Lake Washington	.02	Chen and Orlob (1975)
Various Streams	.042-.125	Hydroscience (1971)
Boise River, Idaho	.02	Chen and Wells (1975)
San Francisco Bay Estuary	.02	Chen (1970)
Long Island Estuaries, New York	.02-.333	Tetra Tech (1976b)

TABLE 3-27. NUTRIENT K_s VALUES FOR E. COLI (AFTER MITCHELL AND CHAMBERLIN, IN PRESS)

Nutrient	Medium	T °C	K_s Micromoles	Remarks	Reference
Glucose	minimal medium		22.		Monod (1942)
			19.4		
			41.7		Moser (1958)
		30	405.		Schultz and Lipe (1964)
		30	550.		
	seawater	20	44.		Jannasch (1968)
Lactose	seawater	20	50.		Jannasch (1968)
	minimal medium		111.		Monod (1942)
Phosphate	minimal medium		0.7	uptake study	Medveczky and Rosenberg (1970)
	minimal medium	30	17.35		Shehata and Marr (1971)
Glucose		30	0.378		Shehata and Marr (1971)

However, Gaudy, et al. (1971) have shown that the Monod expression (Equation (3-56)) is not adequate to describe transient coliform growth behavior. Accordingly, as suggested by Mitchell and Chamberlin (in press), the utility of the K_s value is in evaluating which nutrient may be growth limiting rather than in estimating a growth rate, μ.

Work on coliforms in the Ohio River by Frost and Streeter (1924) revealed that the log decay rate for coliforms is nonlinear with time. Accordingly, use of a simple decay expression such as Equation (3-54) with a single value of k is only an approximation to the actual die-off process. Such an approach must, to some extent and as a function of time, overestimate and/or underestimate dC/dt. One approach to solving the problem of a time-variable decay rate is to decompose the death curve into two components, each having its own decay rate (Velz, 1970). This approach is predicated upon typical death rate curves such as those shown in Figure 3-9. These curves have essentially two regions, each with its own characteristic slope, and the coliform concentration as a function of time may be defined as:

$$C_t = C_o e^{-kt} + C_o' e^{-k't} \tag{3-57}$$

where C_t = coliform concentration at time t, mg/l

C, C_o' = concentrations of each of the two hypothetical organism types, mg/l

k, k' = decay rates for the two organism types, day^{-1}

Table 3-28 shows values for C_o, C_o', k, and k' for E. coli as estimated by Phelps (1944).

TABLE 3-28. VALUES OF C_o, C_o', k, AND k' FROM THE OHIO RIVER (PHELPS, 1944)

Parameter	Warm Weather	Cold Weather
C_o (percent)	99.51	97
k (day), base e	1.075	1.165
Half-life (day)	.64	.59
C_o' (percent)	.49	3.0
k' (day), base e	.1338	.0599
Half-life (day)	5.16	11.5

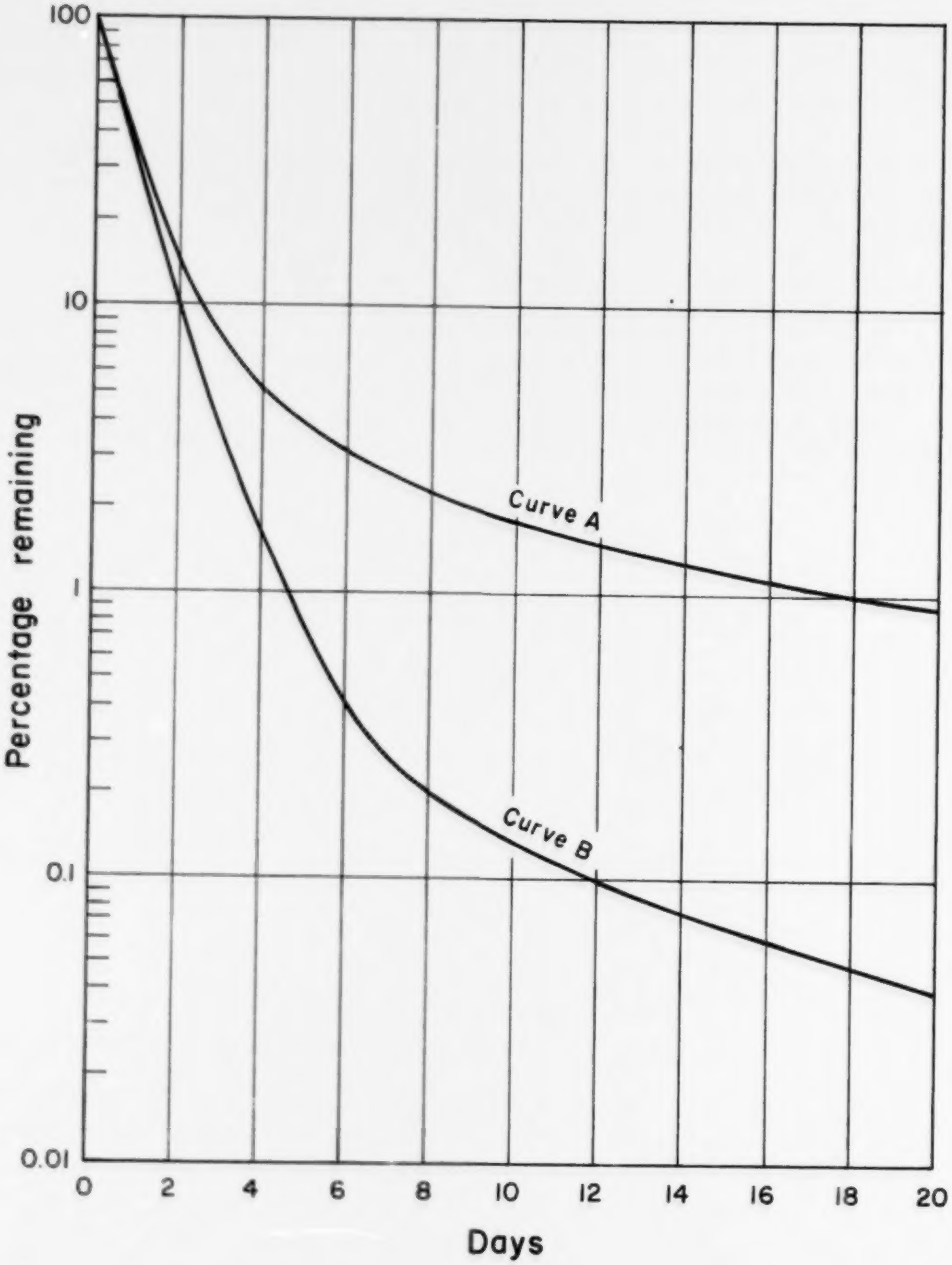

Figure 3-9. Typical mortality curves for coliforms as a function of time. Curve A is for cool weather while curve B represents warm weather decay (redrawn from Velz, 1970).

Lombardo (1972), in an effort to more meaningfully model coliforms, has formulated the dynamics of the coliform population plus streptococci with three separate first order expressions:

$$C_{T_t} = C_{T_o} e^{-k_T t} \tag{3-58}$$

$$C_{f_t} = C_{f_o} e^{-k_f t} \tag{3-59}$$

$$C_{s_t} = C_{s_o} e^{-k_s t} \tag{3-60}$$

where C_t = organism concentration at time t, mg/l

C_o = organism concentration at time zero, mg/l

Subscript T represents total coliforms,
f represents fecal coliforms, and
s represents fecal streptococci

Table 3-29 provides data for k_T, k_s and k_f as provided by Lombardo (1972).

As discussed earlier, recent studies have suggested that incident light levels strongly affect coliform die-off rates. Chamberlin and Mitchell (in press) have defined a light level-dependent die-off rate coefficient as

$$k' = k_\ell \, \ell_o e^{-\alpha z} \tag{3-61}$$

where k' = the light dependent coliform die off rate, 1/hr

k_ℓ = proportionality constant for the specific organism, cm^2/cal

ℓ_o = incident light energy at the surface, cal/cm^2-hr

α = light attenuation coefficient per unit depth (see Section 2.3.5)

z = depth in units consistent with α

TABLE 3-29. RATE OF DISAPPEARANCE OF COLIFORM AND FECAL STREPTOCOCCUS BACTERIA (FROM LOMBARDO, 1972)

Bacteria	Reference	K 1/hr	Remarks
Fecal Coliform	Geldreich, et al. (1968)*	0.0105	Average value for stormwater runoff stored at 10°C for 14 days
Fecal Coliform	Geldreich, et al. (1968)*	0.0654	Average value for stormwater runoff stored at 20°C, 1st day
Fecal Coliform	Geldreich, et al. (1968)*	0.0413	Average value for stormwater runoff stored at 20°C, 2nd day
Fecal Coliform	Geldreich, et al. (1968)*	0.0259	Average value for stormwater runoff stored at 20°C, 3rd day
Fecal Coliform	Geldreich, et al. (1968)*	0.0134	Average value for stormwater runoff stored at 20°C, 4th-7th day
Fecal Coliform	Geldreich, et al. (1968)*	0.0076	Average value for stormwater runoff stored at 20°C, 8th-14th day
Total Coliform	Klock (1971)	0.0288-0.0096	Clean rivers and lakes
Total Coliform	Klock (1971)	0.0384-0.0144	Polluted rivers and lakes
Total Coliform	Evans, et al. (1968)	0.0384	Stormwater runoff, initial regrowth
Total Coliform	Evans, et al. (1968)	0.0211	Stormwater runoff, initial die-away
Fecal Coliform	Evans, et al. (1968)	0.0577	Stormwater runoff, initial die-away
Fecal Coliform	Evans, et al. (1968)	0.0481	Stormwater runoff, 24 hours after initial die-away
Fecal Coliform	Evans, et al. (1968	0.0962	Stormwater runoff, 48 hours after initial die-away
Fecal Streptococci	Evans, et al. (1968)	0.0625	Stormwater runoff, initial die-away

(continued)

TABLE 3-29 (continued)

Bacteria	Reference	K 1/hr	Remarks
Fecal Streptococci	Geldreich, *et al.* (1968)*	0.0019	Average value for stormwater runoff stored at 10°C for 14 days
Fecal Streptococci	Geldreich, *et al.* (1968)*	0.0125	Average value for stormwater runoff stored at 20°C, 2 days
Fecal Streptococci	Geldreich, *et al.* (1968)*	0.0065	Average value for stormwater runoff 20°C, 3rd day
Fecal Streptococci	Geldreich, *et al.* (1968)*	0.0044	Average value for stormwater runoff 20°C, 4th-14th day
Fecal Coliform	CDWR (1962)	0.13	Unchlorinated primary domestic effluent discharged nearby, average rate in June
Total Coliform	CDWR (1962)	0.1053	Unchlorinated primary domestic effluent discharged nearby, average rate in June
Total Coliform	CDWR (1962)	0.04	Unchlorinated primary domestic effluent discharged nearby, average rate in October
Fecal Coliform	CDWR (1962)	0.0668	Industrial and primary treatment discharges average rate in June
Total Coliform	CDWR (1962)	0.0223	Industrial and primary treatment discharges average rate in June
Total Coliform	CDWR (1962)	0.0182	Industrial and primary treatment discharges average rate in October
Fecal Coliform	CDWR (1962)	0.0419	Many small secondary treatment effluents, large chlorinated primary treatment effluent and sugar beet wastewater from August to December. initial rate in June

(continued)

TABLE 3-29 (continued)

Bacteria	Reference	K 1/hr	Remarks
Total Coliform	CDWR (1962)	0.0425	Many small secondary treatment effluents, large chlorinated primary treatment effluent and sugar beet wastewater from August to December. Initial rate in June
Total Coliform	CDWR (1962)	0.051	Many small secondary treatment effluents, large chlorinated primary treatment effluent and sugar beet wastewater from August to December. Average rate in August
Fecal Coliform	CDWR (1962)	0.0542	Many small secondary treatment effluents, large chlorinated primary treatment effluent and sugar beet wastewater from August to December. Average rate in August
Total Coliform	CDWR (1962)	0.0293	Many small secondary treatment effluents, large chlorinated primary treatment effluent and sugar beet wastewater from August to December. Initial rate in October
Total Coliform	CDWR (1962)	0.0889	Cited results of lower Illinois River, summer, first 20 hours travel from peak population
Total Coliform	CDWR (1962)	0.0761	Cited results of lower Illinois River, summer, 21st to 30th hours of travel from peak population
Total Coliform	CDWR (1962)	0.0374	Cited results of lower Illinois River, summer, 31st to 50th hour of travel from peak population

*Note that Lombardo (1972) does not reference Geldreich, *et al.* 1968. The reader is referred to Lombardo where several references to Geldreich are listed.

Then, incorporating the vertical dispersion of bacterial cells,

$$\frac{\partial C(z,t)}{\partial t} = E_z \frac{\partial^2 C(z,t)}{\partial z^2} - k' C\,(z,t) \qquad (3\text{-}62)$$

where E_z = the vertical dispersion coefficient, cm^2/hr

An expression of this kind is useful where the vertical distribution of coliforms is nonuniform over depth and where die-off is assumed to be solely a function of light intensity.

According to Chamberlin and Mitchell (in press), if the bacterial cells can be assumed uniform over depth (i.e., the water column is vertically mixed), then the depth-averaged light intensity and the depth-averaged decay rate, respectively, may be computed:

$$\overline{\ell} = \ell_o \left(\frac{1-e^{-\alpha H}}{\alpha H} \right) \qquad (3\text{-}63)$$

and

$$\overline{k} = k_\ell \overline{\ell} \qquad (3\text{-}64)$$

where $\overline{\ell}$ = the depth-averaged light intensity, cal/cm^2-hr

H = the depth of the water column in units consistent with α

$\overline{k}$ = the depth-averaged light-dependent die-off rate, hr^{-1}

The depth-averaged, light-dependent die-off rate, $\overline{k}$, may be used in the first order die-off expression for a vertically mixed water body so that

$$\frac{dC}{dt} = \overline{k}C \qquad (3\text{-}65)$$

It is clear that the use of such a model (Equation (3-65)) might be further refined by computing $\overline{k}$ using a sinusoidal function to estimate light levels and incorporating the influence of such factors as latitude, day of the year, time of day, and atmospheric conditions including cloud cover and dust effects. Table 3-30 presents some values for k_ℓ.

TABLE 3-30. COMPARISON OF k_ℓ ESTIMATES (AFTER CHAMBERLIN AND MITCHELL, IN PRESS)

Organism	Study	k_ℓ (cm^2/cal)	Data Source
Coliform group	14 Field Studies		Gameson and Gould (1975)
	Mean	0.481	
	5%'tile	0.163	
	95%'tile	1.25	
	24 Field Studies		Foxworthy and Kneeling (1969)
	Mean	0.168	
	5%'tile	0.068	
	95%'tile	0.352	
	61 Laboratory Studies		Gameson and Gould (1975)
	Mean	0.136	
	5%'tile	0.062	
	95%'tile	0.244	
Escherichia coli	4 Field Studies		Gameson and Gould (1975)
	Mean	0.362	
	Min	0.321	
	Max	0.385	
	4 Laboratory Studies		Gameson and Gould (1975)
	Mean	0.354	
Seratia marcescens	4 Field Studies		Gameson and Gould (1975)
	Mean	0.192	
	Min	0.093	
	Max	0.360	
Bacillus subtilis var. niger	1 Laboratory Study	0.002	Gameson and Gould (1975)

(continued)

TABLE 3-30 (continued)

Organism	Study	k_ℓ (cm^2/cal)	Data Source
Fecal Streptococci	3 Laboratory Studies		Gameson and Gould (1975)
	Min	0.048	
	Max	0.123	
	3 Field Studies	0.000	Gameson and Gould (1975)
	1 Field Study	0.007	
	12 Field Studies, initial rates		Foxworthy and Kneeling (1969)
	Mean	0.091	
	Min	0.004	
	Max	0.184	
Salmonella typhimurium	2 Laboratory Studies	1.48 6.40	Eisenstark (1970)

3.8.3.3 Methods of Measurement

Estimates of the coliform die-off rate, k, may be obtained in a number of ways in the laboratory or, preferably, in situ. For laboratory estimates, samples of effluent may be taken along with samples of receiving water. Then, under controlled conditions of light, temperature, and dilution, the time rate of die-off may be determined for various combinations of conditions.

In situ, k values can be determined whether the flow regime is well defined or not, although there are inherent errors involved in each method. Where there are no flow regime data, or where flows are of a transient nature, a commonly used method is to add a slug of a conservative tracer substance (a dye, rare element, or radioisotope) to the steady-state discharge. Then the discharge plume is sampled, dilution is estimated from concentrations of tracer, and the dilution corrected coliform counts permit k to be estimated. It should be recognized that this technique may give misleading results where the dilution of the tracer is due to mixing with water heavily contaminated with the same discharge. Since the tracer had been introduced as a slug, there is no way to know how much of the surviving coliforms originated in the tracer-dosed effluent and how much came from predosing or post-dosing effluent. However, where the flow regime is sufficiently predictable and stable to assure that dilution occurs essentially with ambient water, and where coliform levels in the ambient water are known, this should not be a problem.

Another method, which is particularly useful where discharge is to a channel, is as follows. First, a base sampling site is established below the discharge where the water column is fully mixed normal to the direction of flow. Then samples are taken at the base site and at several points downstream. Based upon known velocities and the change in coliform concentration with distance (time), k values may be estimated. Clearly, errors will be introduced to the extent that there is incomplete lateral mixing of the stream, nonuniform longitudinal velocities laterally and vertically across the channel, and unknown inflows causing dilution or introducing additional coliforms between sampling sites. Also, sampling can be done so that the same "parcel" of water is sampled, in case the discharge is not at steady-state. For example, if the first sampling site is one mile below the base site, and the channel flow has a mean velocity of 2 feet per second, then the first sampling site should be sampled

$$\frac{5280\text{ ft}}{\text{mile}} \times \frac{1\text{ second}}{2\text{ feet}} \times \frac{1\text{ hr}}{3600\text{ seconds}} = .73\text{ hr}$$

or 44 minutes after sampling at the base site. Clearly, however, this does not account for dispersion, and the 44 minutes is an average figure corresponding to the peak loading. Where possible, dye studies or other technique should be used to characterize stream dispersion at the sampling location. Then, by integrating under the curve, total surviving coliforms can be estimated. If, on the other hand, discharge and stream conditions are clearly at steady-state, sampling times are of no consequence.

Equation (3-66) may be used to estimate k where a slug dose of tracer has been introduced into the discharge (assuming first order decay).

$$k = -\ell_n \left(C_t\ F_o/F_t\ C_o\right)/t \qquad (3\text{-}66)$$

where F_o = discharge concentration of tracer, mg/l

F_t = observed concentration of tracer, mg/l

If no tracer is used and conditions exist approximating plug flow, then:

$$k = -\ell_n \left(C_t/C_o\right)/t \qquad (3\text{-}67)$$

where C_o = concentration of coliforms at the base sampling site, mg/l

Regardless of the technique used for estimating k, it is important to concurrently quantify, to the extent possible, those variables which influence k. For example, light levels should be measured or at least estimated over the period for which k is estimated. If this is not done, and if the effects of the important parameters are not taken into account in modeling coliforms, serious errors will result. Table 3-31 shows how serious such errors can be. The data show T-90 values for coliforms as a function of incident light. T-90 values are the times required for 90 percent mortality. The associated k values are .058 hr^{-1} in the dark and .1 hr^{-1} at midday. It is clear that estimating a single value for k could result in greater than order-of-magnitude errors.

3.8.4 Summary

Coliforms are of interest as an index of pathogen contamination in surface waters, and the group of organisms has become one of the most commonly modeled water quality parameters. Modeling coliforms usually encompasses the use of a simple first order decay expression to describe die-off. Since regrowth is generally conceded as unimportant, no growth terms are normally included in the model.

The die-off rate, k, is a function of a number of variables, the effects of all of which are not well understood. It now appears that light (in the visible range) is important as are a number of physicochemical factors and the presence of heavy metals. Rates of die-off are also sensitive to the salinity of the water, this also affecting the influence of light on die-off rates.

TABLE 3-31. EXPERIMENTAL HOURLY T-90 VALUES (AFTER WALLIS, ET AL., 1977)

Time of Day	T-90 (hours)	Time of Day	T-90 (hours)	Time of Day	T-90 (hours)
0100	40	0900	3.2	1700	5.3
0200	40	1000	2.5	1800	6.7
0300	40	1100	2.3	1900	8.5
0400	40	1200	2.5	2000	11
0500	40	1300	2.9	2100	14
0600	19	1400	3.3	2200	20
0700	8.0	1500	3.9	2300	27
0800	4.6	1600	4.6	2400	34

3.8.5 References

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3.9 ALGAE

3.9.1 Introduction

Water column algal populations have historically been among the most commonly simulated water quality parameters. This has been the case for a number of reasons. These include:

- Algal metabolism can strongly affect other water quality parameters such as:

    - Dissolved oxygen
    - BOD
    - Nutrient levels
    - pH
    - Turbidity

  In some cases, particularly with regard to DO, phytoplankton can cause great diurnal fluctuations.

- Algae are an important component of the primary producers, particularly in lake ecosystems. They are an important factor in understanding eutrophication status and processes.

- Algae affect tastes and odors in potable water supply. Under some conditions, they may cause problems in use of water for industrial processes.

- Significant algal blooms can affect use of waters for recreation.

This section is devoted to the formulations and rate constants used in simulating algal population dynamics. Although many different approaches have been taken in the past, a commonly used general approach has developed. This approach is emphasized in this section, along with information relating to the algal specific growth rate, the algal endogenous respiration rate, algal settling, and the Michaelis-Menton half-saturation constants as they relate to algal population dynamics.

It is very important to recognize that many models, which purport to simulate "algae" actually seek to predict some composite behavior. Invariably, although there may be relatively few dominant algal species present in the water column at a point in time, this dominance, and indeed the entire plankton species profile is capricious. Accordingly, not only is it a gross approximation to simulate the algal assemblage as a single alga, but perhaps even more important is the error inherently introduced by using constant rates in long time-period simulations. The various rates are highly species and temperature dependent. Accordingly, while selected rate constants may be satisfactory over some short period of time, they may introduce serious simulation errors where prototype conditions are changing substantially.

It should also be noted that no distinction is made in many models as to the physical characteristics of the "alga." In general, relationships to be discussed are for phytoplanktonic forms.

The basic approach to simulating phytoplankton in many popular models is founded upon the expression:

$$\frac{dP}{dt} = \left(G_p - D_p \right) P \qquad (3\text{-}68)$$

where G_p = specific growth rate, day^{-1}

D_p = specific death rate, day^{-1}

P = phytoplankton concentration, mg/l

The fundamental equation is usually expanded to account for the effects of growth-limiting conditions, respiration, predation, and settling. In order to incorporate the effects of growth limiting conditions, the maximum specific growth rate is modified. Commonly this is done in a fashion analogous to:

$$G_p = MK_p(T) \qquad (3\text{-}69)$$

where M = Monod type half-saturation expression for the growth limitation terms for nutrients, light, and temperature, unitless.

G_p = specific growth rate, day^{-1}

$K_p(T)$ = Temperature-dependent maximum-specific growth rate, day^{-1}

The specific death rate (D_p) may be separated into a respiration term, a predation term, and a settling term:

$$D_p = R_p + S_p + F_p \qquad (3\text{-}70)$$

where R_p = respiration rate, day^{-1}

S_p = settling rate, day^{-1}

F_p = predation rate, day^{-1}

The equation becomes:

$$\frac{dP}{dt} = \left(MK_p(T) - R_p - S_p - F_p\right) P \qquad (3\text{-}71)$$

3.9.2 Phytoplankton Specific Growth Rate (G_p)

3.9.2.1 Factors Affecting G_p

As discussed above in general terms, there are several factors which can limit or at least mediate the rate of phytoplankton growth. These are:

- Availability of nutrients
- Light levels
- Temperature
- Availability of silica (diatoms)

It is very clear that some factor or factors must provide a limitation on the rate of growth and replication of algal cells. Obviously, in theory, environmental factors may be optimal and may not provide such limitation. In this case the biochemistry of the organism determines the rate of growth and replication, and the rate is the maximum or saturated growth rate, K_p. In natural systems, however, non-optimal levels of one or more factors or substances required for growth are likely to cause the rate to be less than K_p.

A large body of research and literature has been developed over recent years regarding growth limitation in natural water bodies. There is some evidence that more than half of the lakes in the U.S. east of the Rockies are phosphorus limited (Gakstatter, et al., 1975)*. Studies performed by Maloney, et al. (1972) on waters from nine Oregon lakes (in-vitro studies) have shown that in four lake samples, phosphorus addition alone greatly stimulated algal growth. The addition of nitrogen alone stimulated algal growth slightly in two lakes. In one lake, which was highly oligotrophic (severe deficiency of one or more nutrients), the addition of nitrogen, phosphorus, and carbon had no effect on algal growth rates.

Powers, et al. (1972) reported in situ studies on natural algal populations in Minnesota and Oregon. In Shagawa Lake in Minnesota, additions of phosphorus, of nitrogen, and of both nitrogen and phosphorus elicited increases in algal growth rates, thus suggesting that the concept of a single growth limiting substance must be expanded to accommodate limitation by a combination of substances or factors. In Burntside River in Minnesota, Powers, et al. (1972) found that algal growth was stimulated only when phosphorus and nitrogen were added in combination. Algal growth in moderately productive Triangle Lake was stimulated by the addition of phosphorus and further stimulated by the addition of phosphorus plus nitrogen.

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*According to Lorenzen (pers. comm.), the concept of limitation of growth is often misinterpreted, and results of studies commonly reflect laboratory conditions rather than lake algal dynamics.

Schelske and Stoermer (1972) have found significant correlations between particulate phosphorus and the rate of carbon fixation in Lake Michigan. Based upon enrichment experiments conducted in 1970, phosphorus was found to be limiting, while nitrogen was not limiting.

Welch, et al. (1973) have discussed the trophic status of Lake Washington and Lake Sammamish in the State of Washington. Results of nutrient diversion from the lakes have shown that while diversion has led to a decrease in productivity in Lake Washington, and suggest that this lake is phosphorus limited, diversion of phosphorus has not substantially affected productivity in Lake Sammamish. Welch, et al. suggest that the phosphorus change in Lake Sammamish has occurred on the asymptotic part of the response curve. Although this might appear tantamount to saying that Lake Sammamish is not phosphorus limited, Welch, et al. also suggest that the availability of phosphorus is mediated by iron released from sediments below an anaerobic hypolimnion. The iron reacts with phosphorus, making it unavailable as a nutrient, and deposits the phosphorus in the sediment. If the level of phosphorus were increased significantly, the authors argue, the production rate would also increase. This means that the lake is phosphorus limited to an extent, but the effect on production of short-term, small scale changes in phosphorus is masked by the dynamic behavior of sediment phosphorus exchange.

Much of the literature has emphasized phosphorus and nitrogen studies, and research done in recent years has suggested that phosphorus is more often limiting than nitrogen. Very much less often, studies are conducted to determine the extent to which carbon is limiting. Kerr, et al. (1972), for example, investigated the role of nitrogen, phosphorus, and carbon in Shriner's Pond, a small fishpond in Georgia. Their findings suggest that while nitrogen, phosphorus and potassium additions to the pond caused increased algal production, the carbon content also influenced the rate of production. Powers, et al. (1972) found that carbon increased productivity in one instance when added with nitrogen and phosphorus to Burntside River. In another case, moderately productive Triangle Lake exhibited increased productivity through the addition of carbon. Overall, it appears that while carbon may not be as important as either phosphorus or nitrogen, it probably plays a significant role in algal growth regulation in a limited number of surface waters.

In addition to the macronutrients (i.e., phosphorus, nitrogen, potassium, carbon), micronutrients (i.e., essential metals, sulfur) may be limiting under certain conditions, particularly in oligotrophy. Goldman (1972), for example, found that significant trace element deficiencies existed in 82 percent of the 28 oligotrophic lakes he studied. In ten lakes in New Zealand, the addition of cobalt, iron, zinc, manganese and molybdenum elicited phytoplanktonic responses ranging from maxima of less than a ten percent increase in productivity to one case of more than an 80 percent increase. Goldman also obtained positive responses from trace element additions to lakes in Alaska (molybdenum, cobalt, manganese, zinc individually), Africa (iron and various combinations of nitrogen, sulfur, potassium, and phosphorus in eutrophic Lake George) and California (Lake Tahoe and others, addition of iron, zinc, and manganese individually).

Algal growth limitation by non-optimal light levels has been extensively investigated both *in situ* and *in vitro*. Light provides the energy in the carbon fixation process which uses carbon dioxide and water in the green plant cell biosynthesis of glucose, glucose polymers (cellulose, starches, various sugars), and other energy storing substances along with some amino-acids. The energy stored in the photosynthesis process, of course, provides the energy for cellular active transport, respiration, biosynthesis, and other energy consuming processes vital to the algal cell.

In view of the role of light in cellular energetics and biochemical synthesis, substantial changes in light levels must have a very major effect on algal cell function in general and growth rates in particular. In a study by Stepanek (1969), a close statistical relationship between the duration of sunshine and the numbers of nannoplankton produced in Sedlice Reservoir was found ($r = .929$). Stepanek also examined statistical relationships between numerical productivity and solar azimuth and blue-violet, and total visible components of incident solar radiation. Generally, the correlation coefficients were reasonably high with $r^2 > .64$ in all but the correlation between total visible radiation and numerical productivity ($r^2 \simeq .42$).

Jorgensen and Steeman-Nielsen (1969) have discussed rates of photosynthesis in *Skeletonema costatum* (a diatom) as a function of light level and adaptation period. According to their data, at 8°, 14°, and 20°C, the photosynthetic rate (carbon fixation per cell per hour) is essentially constant in the range 15K to 30K lux. The rate is greatest at 20 degrees. In the range from about 8 to 15 degrees, the rate of photosynthesis increases, but at a decreasing rate. In the range 0 degrees to about 8 degrees, the photosynthetic rate increases linearly, with a slope of about 2.3×10^{-7} μgC/cell-hour-lux. The daily growth rate at 10K lux was 3.7 for cells adapted to 8°C compared with 5.4 for 20°C adapted cells. Jorgensen and Steeman-Nielsen also suggest that *S. costatum* cells grown with a short light period synthesize and maintain a higher level of photosynthetic pigments than cells grown with a short dark period. The short light period grown cells also show by far the highest photosynthetic rate (by about a factor of 1.5 in the range 10K to 30K lux).

Thomas (1966) has studied the effects of illuminance on three species of oceanic phytoplankton. Figure 3-10 shows the effects of light levels on two forms of *Gymnodinium*. Figure 3-11 shows similar curves for *Nannochloris* and *Chaetoceros* species. Table 3-32 shows optimal growth illumination using various measures as criteria (Brown and Richardson, 1968). Figures 3-10 and 3-11 show that up to about 400 foot candles, the change in phytoplankton growth rate is approximately linear. Between

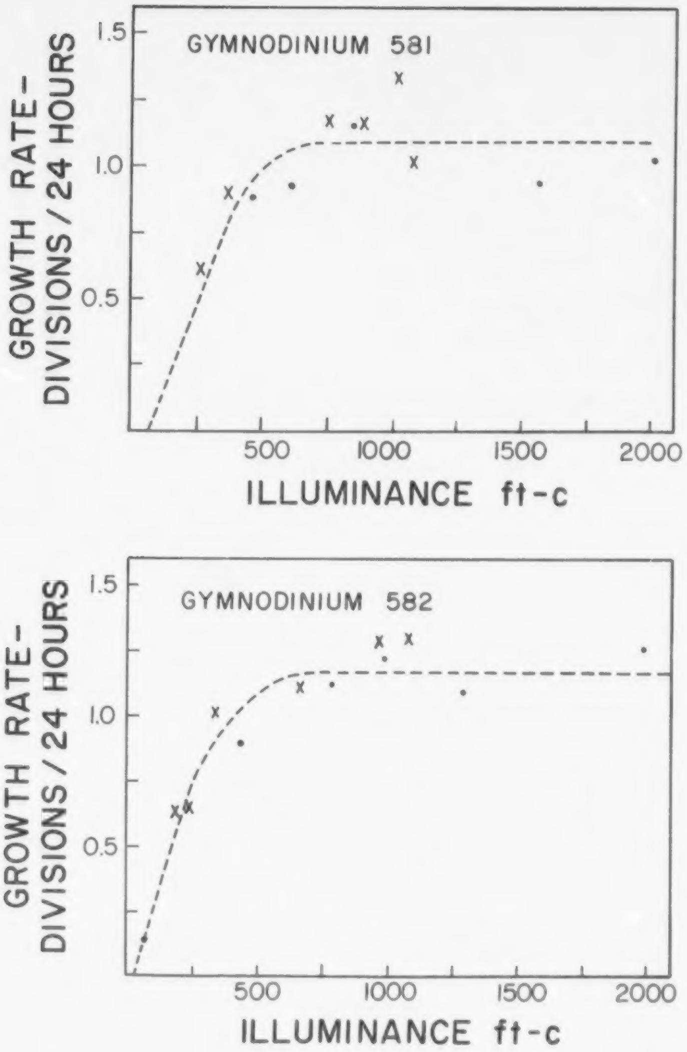


Figure 3-10. Effect of light levels on growth rates of *Gymnodinium* (Thomas, 1966).

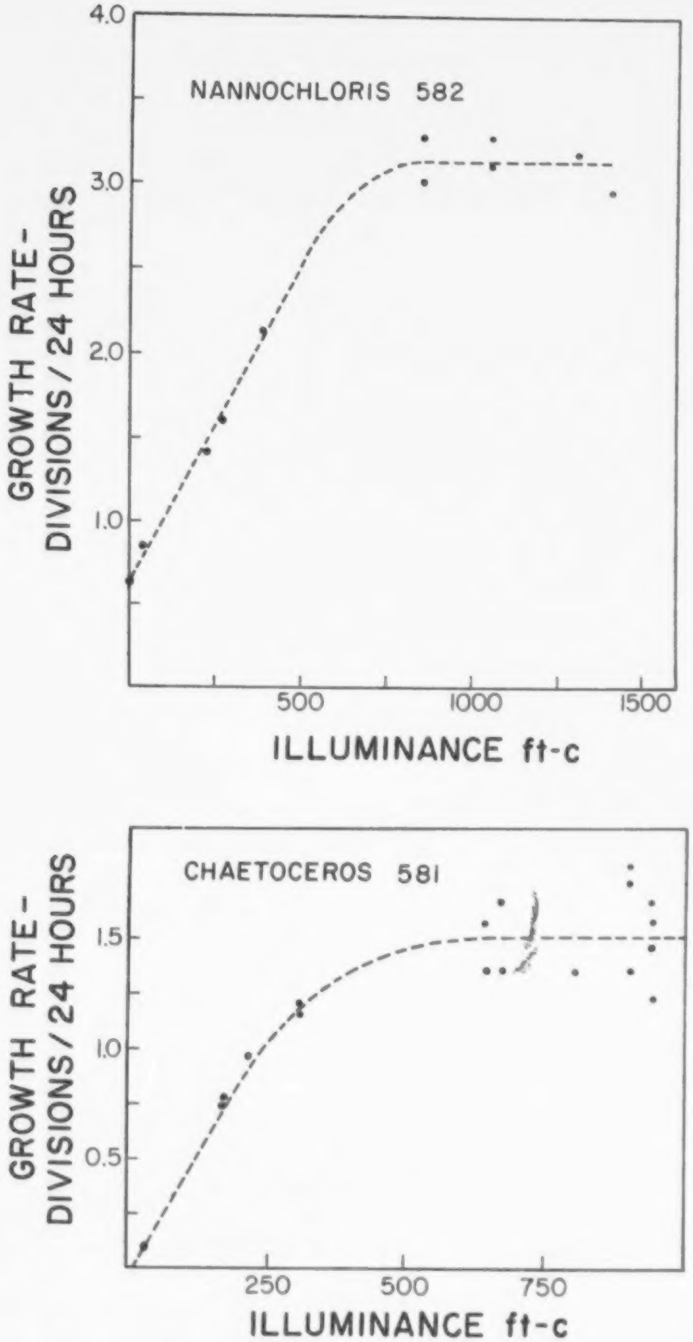


Figure 3-11. Effects of light levels on growth rate of Nannochloris and Chaetoceros (Thomas, 1966).

TABLE 3-32. OPTIMAL GROWTH ILLUMINATION (ALL VALUES IN FT-C) FOR VARIOUS MEASUREMENTS (BROWN AND RICHARDSON, 1968)

	Growth	DT hr*	P_s	Res	Q-Hill	Pigmentation	Cell Volume	
							Max.	% Max.Inc.
Cyanidium caldarum	400	77	<50	-	<50	<50	>1000	>100
Gloeocapsa alpicola	400	29	>1150	700	100-400	<50	800	150
Phormidium luridum	500	18	<50	150	<75->1300	500	-	-
Phormidium persicinum	200	24	400	>600	-	200	-	-
Porphyridium aerugineum	400	37	<50	200	150	<50	600	210
Porphyridium *cruentum*	800	21	50	-	400	150	400	190
Astasia longa	200-1000	21	-	1200	-	-	<50	30
Amphidinium sp.	600	48	>1200	>1200	<50	90	<50	59
Cryptomonas ovata	>1000	22	250	500	<25	250	-	-
Nitzschia closterium	400->1100	48	>1100	>1100	<50	<50	<50	120
Ochromonas danica	700	12	>1350	>1350	400	400	<25	47
Sphacelaria sp.	200-600	30 days	<50	300	<50	<50	-	-
Chlorella pyrenoidosa	>2750	13	400-1300	800	400	400	250	1800
Chlorococcum wimmeri	>1000	67	>1000	>1000	400	Chloro.<50 Asta.>1000	400	110
Euglena gracilis	>1100	26	400	>1100	100	175	>1100	80
Tribonema aequale	800	18	>1300	>1300	100	no max.	-	-

*Doubling time (DT) refers to the time required for the population of 1-liter cultures to increase 100%. Lower DT periods are readily obtained for short periods with small volumes of dilute cell suspensions. Doubling time is measured at the initial point of greatest growth.

P_s = photosynthetic rate, Res = respiration, Q-Hill - quinone-hill reaction.

about 400 and 700 foot candles, growth increases at a decreasing rate with increased illuminance, and above about 700 foot candles, increased light has little or no effect on growth rate. It should be noted, however, that illuminance levels can be substantially higher than those represented in the figures. At higher levels photoinhibition may occur. In impoundment depth profiles of chlorophyll-a concentrations, in conjunction with decreased growth rates caused by low light levels at greater depth, this phenomenon gives rise to characteristic subsurface bell-shaped curves.

The literature is replete with studies of photosynthetic rates as a function of depth below the water surface. Such studies show the effects of stratification, light attenuation, and/or temperature. Temperature effects on algal growth rates are essentially due to the effect of temperature on chemical reaction rates. Since biochemical reactions are enzyme catalyzed, effects of temperature on algal growth rates reflect the effects of temperature on enzyme molecule characteristics and integrity. According to data from West and Todd (1966), given temperature correction Equation (3-72),

$$K_T = K_{T_r} \theta^{(T-T_r)} \tag{3-72}$$

where T = ambient temperature, °C

T_r = reference temperature, °C

K_T = enzyme catalyzed reaction rate at temperature T, day^{-1}

K_{T_r} = enzyme catalyzed reaction rate at the reference temperature, T_r, day^{-1}

θ = characteristic constant

θ can range from 1.01 to 1.18, for T and T_r within the normal enzyme temperature range. A temperature increase of 15°C, which commonly about doubles reaction rates in uncatalyzed organic reactions, can result in a 1.2 to 12-fold increase in enzymatic reaction rate. Accordingly, algal growth rates are quite sensitive to temperature.

Smayda (1969a) studied the effect of temperature (and light levels and salinity) on a marine diatom, *Detonula confervacea*. Figure 3-12 shows some of Smayda's results.

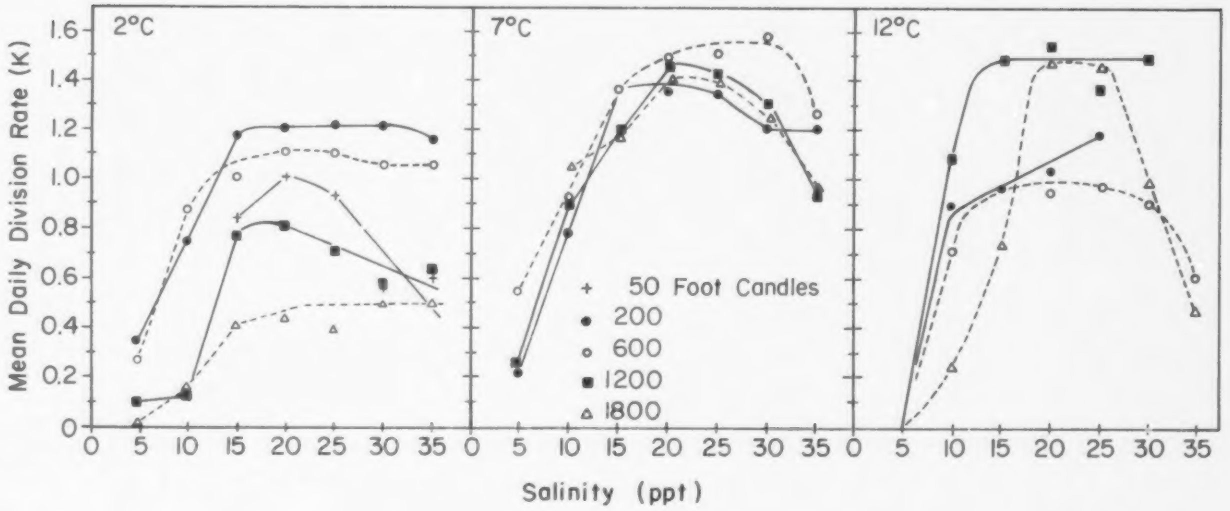


Figure 3-12. The mean daily division rate of Detonula confervacea grown for six days at various combinations of light, temperature, and salinity, following preconditioning at these experimental conditions (after Smayda, 1969a).

3.9.2.2 Applications and Modeling Approaches

3.9.2.2.1 General Discussion of G_p and Use of the Michaelis-Menton Formulation

Several approaches are commonly used to describe the specific growth rate G_p (or μ). This rate is known to be a function of temperature, light, and nutrient concentration as discussed above. Numerous investigators (see, for example, Baca and Arnett, 1976; U.S. Army Corps of Engineers, 1974; Canale, *et al.*, 1976; and O'Connor, *et al.*, 1975) have used a specific growth rate formulation of the following general form:

$$G_p = K_p(T)\ r\left(I_s, K_e\right) \prod_{i=1}^{n} \left(C_i / \left(K_{m,i} + C_i\right)\right) \qquad (3\text{-}73)$$

where $K_p(T)$ = saturated growth rate, a function of temperature, day^{-1}

$r(I_s, K_e)$ = light reduction term due to non-optimal incident light, a function of the saturated light intensity, I_s, and the extinction coefficient, K_e, unitless

i = subscript representing each of the n specific nutrients with potential to limit growth (primarily nitrogen and phosphorus, and sometimes carbon and silicate)

$K_{m,i}$ = the ith Michaelis-Menton or half-saturation constant, mg/l

C_i = the ith nutrient concentration, mg/l

Tetra Tech (1975, 1976) and the U.S. Army Corps of Engineers (1974) have used the following growth expression:

$$G_p = \left[K_T\ \theta^{(T-20)}\right] \left[\frac{LI}{L_2+LI}\right] \left[\frac{PO_4}{P_2+PO_4}\right] \left[\frac{CO_2}{C_2+CO_2}\right] \left[\frac{N}{N_2+N}\right] \qquad (3\text{-}74)$$

where K_T = maximum specific growth rate at 20°C, days^{-1}

θ = temperature coefficient, ranging from 1.02-1.06

P_2 = half-saturation constant for algae utilizing phosphorus, mg/l

N_2 = half-saturation constant for algae utilizing nitrogen, mg/l

C_2 = half-saturation constant for algae utilizing carbon, mg/l

L_2 = half-saturation constant for algae utilizing light energy, kcal/m^2-sec

PO_4, N, CO_2 = concentrations of phosphorus, nitrogen, and carbon dioxide, respectively, mg/l (or consistent units with P_2, N_2, and C_2)

LI = incident light level in kcal/m^2-sec

The variable LI refers to the available light intensity, which is known to vary as a function of both depth and time. This parameter is discussed in detail elsewhere in this report (Section 2.3.5).

Chen and Orlob (1975) and Chen and Wells (1975) used this same formulation for the specific growth rate in model applications to Lake Washington, San Francisco Bay Estuary, and Boise River, Idaho.

The Michaelis-Menton half-saturation constants are commonly used to adjust the growth rate of phytoplankton (or other forms) to suboptimal levels of potentially growth limiting factors. Such factors include nutrients and light. Each constant is actually the level at which the particular factor limits growth to half the maximal or "saturated" rate.

Thomann, Di Toro, and O'Connor (1974) formulated the phytoplankton growth expression in a similar fashion as follows:

$$G_{p_j} = K_T \cdot T \cdot \left(\frac{2.718\ f}{K_e\ H} \left(e^{-\alpha_1} - e^{-\alpha_o} \right) \right) \left(\frac{N}{K_n + N} \right) \left(\frac{D}{K_D + D} \right) \qquad (3\text{-}75)$$

where G_{p_j} = growth rate averaged over depth

K_T = maximum growth rate, days^{-1}°C^{-1}

T = temperature, °C

f = photoperiod; ranging from 0.3-0.7 (fraction of a day, unitless)

K_e = extinction coefficient; ranging from 0.1-3.0 m^{-1}

H = depth, m

$\alpha_1 = \frac{I_a}{I_s} e^{-K_e H}$

$\alpha_o = \frac{I_a}{I_s}$

I_s = saturation light intensity, foot candles

I_a = incident light, foot candles

N = nitrogen concentration, mg-N/l

D = phosphorus concentration, mg-P/l

K_n, K_D = half-saturation constant for total inorganic nitrogen and total phosphorus, respectively, mg/l

Thomann, Di Toro, and O'Connor (1975) incorporated a nonlinear temperature maximum growth rate where the temperature correction is made as in Equation (3-72). Here, θ was set equal to 1.066 with a reference temperature of 0°C.

Baca and Arnett (1976) have applied an algal growth rate related to the concentration of the principal nutrients, nitrogen and phosphorus, using a modified Michaelis-Menton expression. The nutrient term formulation is given as:

$$\text{MIN}\left[\frac{C_n}{K_n + C_n}, \frac{D_1}{K_p + D_1}\right] \tag{3-76}$$

where C_n = effective nitrogen concentration, mg/l

K_n, K_p = half-saturation constants for nitrogen and phosphorus, mg/l

D_1 = soluble phosphorus concentration, mg/l

MIN = the minimum value function, $\text{MIN}(A_1, A_2, \cdots, A_n) = A_i \leq A_1, A_2, \cdots, A_n$ where $i = 1, \cdots n$

The effective nitrogen concentration, C_n, is given by:

$$C_n = \left\{ \begin{array}{ll} pC_1 + (1 - p)C_3, & C_1 \text{ and } C_3 > \varepsilon_n \\ C_1 + C_3, & C_1 \text{ or } C_3 \leq \varepsilon_n \end{array} \right\} \tag{3-77}$$

where p = preference factor

ε_n = critical nitrogen level

C_1, C_3 = ammonia and nitrate concentration, mg-N/l

Baca and Arnett (1976) also included a multiplicative term to account for the effect of toxic substances as follows:

$$G_t = \frac{K_t}{K_t + T_c} \tag{3-78}$$

where G_T = Michaelis-Menton growth limitation term due to toxic substance

T_c = concentration of toxic substance, mg/l

K_t = toxicity constant, mg/l

Baca and Arnett (1976) included this toxic substances term in the specific growth expression because they felt that toxic substances generally inhibit growth rates rather than increase respiration (death).

Canale, et al. (1976) is yet another investigator who has employed this type of specific growth formulation. Canale's formulation includes a maximum growth term which is temperature-dependent, a light reduction factor, and a modified Michaelis-Menton expression for nutrient reduction effects. Their nutrient reduction term is formulated much the same way as Baca and Arnett's (1976) expression and, in addition, he includes a multiplicative term for silicate growth limitation (see Sections 2.5.1-2.5.3).

In addition to these more common approaches, other investigators have suggested quite different formulations for specific algal growth, G_p. Bierman's (1976) complex model of phytoplankton-growth kinetics includes four phytoplankton groups: 1) diatoms, 2) greens, 3) non-nitrogen fixing blue-greens, and 4) nitrogen fixing blue-greens. Table 3-33 is a qualitative listing of the operational differences among the four phytoplankton types, as given by Bierman (1976).

TABLE 3-33. QUALITATIVE DIFFERENCES AMONG PHYTOPLANKTON TYPES MODELED BY BIERMAN (1976)

Characteristic Property	PHYTOPLANKTON TYPE Diatoms	Greens	Blue-Green (N-Fixing)	Blue-Green Non N-Fixing)
Nutrient Requirements	P, N, Si	P, N	P, N	P
Relative Growth Rates (optimum at 25°C)	High	High	Low	Low
Phosphorus Uptake Affinity	Low	Low	High	High
Sinking Rate	High	High	Low	Low
Grazing Pressure	High	High	None	None

A unique feature of Bierman's model is that cell growth is considered to be a two-step process involving separate nutrient uptake and cell synthesis mechanisms. Motivation for this variable stoichiometry approach is that an increasingly large body of experimental evidence indicates that the mechanisms of nutrient uptake and cell growth are actually quite distinct (Bierman, 1976). The model includes carrier mediated transport of phosphorus and nitrogen using a reaction-diffusion mechanism, and possible intermediate storage in excess of the immediate metabolic needs of the cell. Specific cell growth rates are assumed to be directly dependent on the intracellular levels of these nutrients, in contrast to the classical Michaelis-Menton approach which relates these rates directly to extracellular dissolved phosphorus.

Bierman (1976) simulated the specific growth rate of phytoplankton, G_p, as the minimum value of the following three functions:

$$G_p = \mathrm{MIN}\begin{cases} G_{max} \cdot f(T) \cdot f(I) \cdot \left[1-\exp(-0.693(P/P_o-1))\right] & (3\text{-}79) \\ G_{max} \cdot f(T) \cdot f(I) \cdot \left[(N-No)/(KNCELL + N-N_o)\right] & (3\text{-}80) \\ G_{max} \cdot f(T) \cdot f(I) \cdot \left[SCM/(KSCM + SCM)\right] & (3\text{-}81) \end{cases}$$

where KNCELL = intracellular half-saturation constant for nitrogen-dependent growth, moles - N/l

KSCM = intracellular half-saturation constant for silicon-dependent growth, moles - Si/l

P = moles phosphorus per phytoplankton cell

P_o = minimum stoichiometric level of phosphorus per phytoplankton cell (mol/cell)

N = moles nitrogen per phytoplankton cell

N_o = minimum stoichiometric level of nitrogen per phytoplankton cell (mol/cell)

SCM = silicon concentration in solution (mol/l)

$f(T)$ = $\theta^{(T-20)}$ where $\theta = 1.07$ for diatoms, 1.08 for green algae, and 1.1 for blue-green algae

T = temperature °C, given by

$$T = \mathrm{TMAX}\left\{0.5-0.5\sin\left[\frac{2\Pi \cdot \mathrm{TIME} + \phi}{360}\right]\right\},$$

value of sin argument in radians

TMAX = maximal water temperature during summer, °C

TIME = day of year, 30 day months

ϕ = -1890. Value gives sin (arg) = 0 for Nov. 1. Nov. 1 = day 301.

$f(I)$ = $\left[1/(ke \cdot \mathrm{DEPTH})\right] \cdot \left[e^{-\alpha 1} - e^{-\alpha o}\right]$

$\alpha 1$ = $(Ia/Is)\, e^{-(ke \cdot \mathrm{DEPTH})}$, unitless

αo = Ia/Is, unitless

ke = (1.9/secchi depth) + .17 · TCROP ≃ .633 + .17 TCROP, m^{-1}

Ia = 2000 ft-C, surface incident light level

Is = saturation light level, ft-C

DEPTH = water column depth, m

TCROP = total phytoplankton biomass, mg dry wt/l

Since the traditional Michaelis-Menton approach to nutrient uptake kinetics does not include a feedback mechanism, Michaelis-Menton kinetics are actually a special case of this two part uptake kinetic theory in which the cell's nutritional state is assumed to be constant.

A major problem in attempting to simulate a complex chemical-biological process is that the models usually contain coefficients for which direct measurements do not exist. It is possible that more than one set of model coefficients could produce an acceptable "fit." In the transition from single-class to multi-class models, this problem becomes particularly acute because it is no longer sufficient to ascertain a range of literature values for a given coefficient. Multi-class models necessitate the definition of class distinctions within this range. Given such circumstances, Bierman (1976) concludes that many of the coefficients in multi-class models simply must be estimated.

The procedure used in Hydrocomp's (Lombardo, 1972) model is to treat the algal uptake of each nutrient separately and then determine which uptake rate causes the smallest phytoplankton growth rate during each time period. Hydrocomp's method assumes a nutrient is limiting for each time period but that the identity of the limiting nutrient may change over successive time periods. This concept, also considered by Bierman (1976) as described previously, has been considered by Orlob (1974) to be a plausible alternative to the single multiplicative Michaelis-Menton formulation.

Hydrocomp's (Lombardo, 1972) expression for phosphate uptake is formulated as:

$$G_{pp} = VMAXP \left(\frac{PO_4}{CMMP + PO_4}\right)\left(\frac{NO_3}{CMMN + NO_3}\right) \qquad (3\text{-}82)$$

where G_{pp} = PO_4 uptake rate, hr^{-1}

VMAXP = maximal PO_4 uptake rate, hr^{-1}; typically 0.3

CMMP = Michaelis constant for phosphorus; typically 0.0303 mg/l

CMMN = Michaelis constant for nitrogen; typically 0.0284 mg/l

PO_4 = PO_4 concentration, mg-P/l

NO_3 = NO_3 concentration, mg-N/l

The PO_4 uptake rate, G_{pp}, may presumably be converted to algal biomass production using chemical equivalence information. Hydrocomp (Lombardo, 1972) assumes a constant chlorophyll-a to phosphorus ratio of 0.6.

The expression used for nitrogen limited growth is given as:

$$G_{pn} = VMAXN \left(\frac{NO_3}{CMMN + NO_3} \right) \qquad (3\text{-}83)$$

where G_{pn} = NO_3 uptake rate, hr^{-1}

VMAXN = maximal NO_3 uptake rate, hr^{-1}; typically 0.7/hr

The following expression is proposed for nitrate uptake under light-limited growth conditions (Lombardo, 1972):

$$G_{pL} = VMAXL \left(\frac{ZI}{CLT + ZI} \right) \qquad (3\text{-}84)$$

where G_{pL} = nitrate uptake rate, hr^{-1}

CLT = Michaelis constant; typically 0.033 langleys/min

ZI = light intensity, langleys/min

VMAXL = maximal NO_3 uptake rate under light-limiting conditions, hr^{-1}; typically 0.3/hr

3.9.2.2.2 Temperature and the Algal Specific Growth Rate

Two notable differences in the growth expression used by Thomann, Di Toro, and O'Connor (1974) and the one used by Chen and Orlob (1975) are the terms for light effects and temperature effects. Thomann, et al., assume a linear relationship between growth rate and temperature while Chen and Orlob apply the temperature correction expression commonly used to adjust temperature-dependent rates:

$$G_p(T) = G_{p(20)}\theta^{(T-20)} \qquad (3\text{-}85)$$

where T = temperature, °C

θ = characteristic temperature correction constant

Baca and Arnett (1976) incorporate a temperature dependent maximum specific growth rate term similar to that of Tetra Tech (1975).

Assuming neither light nor nutrients are in short supply, Lombardo (1972) defines the growth rate to be directly dependent on temperature. The following expression, as suggested by McCombie (Lombardo, 1972), is used:

$$G_p = 0.006T - 0.035 \text{ for: } 28 \geq T \geq 6°C \qquad (3\text{-}86)$$

where G_p = specific growth rate, hr^{-1}

T = water temperature, °C

Lehman, et al. (1975) report another approach to temperature correction of G_p. In their model, which is useful for lakes having ice cover in winter, they assume temperature to be constant over a 24 hour period. For each day during ice-free months, temperature is computed as:

$$T = T_{min} + .5\, T_{max}\left[1 - \text{Cos}\left(2\pi(D - D_m)/(D_e - D_m)\right)\right],\ D_m < D < D_e \qquad (3\text{-}87)$$

where D = day of the year

D_m = day the ice cover melts

D_e = day ice cover is established

T_{min} = minimum yearly epilimnetic temperature, °C

T_{max} = maximum yearly epilimnetic temperature minus T_{min}, °C

Otherwise, $T = T_{min}$. Temperature-dependent relative growth rates (TD) are represented "by skewed normal distributions."

$$TD = \exp\left[-2.3\left[(T - T_{opt})/(T_{u\ell} - T_{opt})\right]^2\right],\ T > T_{opt} \qquad (3\text{-}88)$$

or

$$TD = \exp\left[-2.3\left[(T - T_{opt})/(T_{\ell\ell} - T_{opt})\right]^2\right]\ T \leq T_{opt} \qquad (3\text{-}89)$$

where exp(x) = the exponential function, e^x

T_{opt} = optimal temperature, °C

$T_{\ell\ell}$ = lower limit of T, °C

$T_{u\ell}$ = upper limit of T, °C

Lehman, et al. (1975) suggest that this is an inexact approach to the Arrhenius equation of enzyme activity that Johnson, et al. (1954) suggested may represent the exponential growth phase of microorganism populations.

Lassiter (1975) notes that the approach of Equation (3-85) assumes a monotonically increasing exponential response of the maximal temperature-dependent growth rate to temperature, although this is a reasonable approximation only over a part of the normal temperature range that an algal cell will tolerate. Actually, growth rates have some time-variable optimal temperature remote from which the growth rate drops off very substantially. Lassiter cites a complex set of formulations reported by Bloomfield, et al. (1973) to compute k, a general biotic growth rate (1/day):

$$k = \left(\frac{T_\ell - T}{T_\ell - T_m}\right)^X e^{X\left[1-(T_\ell - T)/(T_\ell - T_m)\right]} \qquad (3\text{-}90)$$

$$X = \left(W^2\left[1 + (1 + 40/W)^{1/2}\right]^2\right)/400 \qquad (3\text{-}91)$$

$$W = \left(\ell n\,(Q_{10})\right)\left(T_\ell - T\right) \qquad (3\text{-}92)$$

$$Q_{10} = \left(K_1/K_2\right)^{\left(10/(T_1 - T_2)\right)} \qquad (3\text{-}93)$$

where T_ℓ = upper limiting temperature at which the growth rate is zero, °C

T_m = optimum temperature for growth, °C

T = ambient temperature, °C

K_1 = reference rate constant, day^{-1}

T_1 = reference temperature, °C

Q_{10} = ratio of rate constants at two temperatures, T_1 and T_2

T_2 = temperature at which K_2 is to be determined, °C

K_2 = computed rate constant at T_2, day^{-1}

This model, as noted by Lassiter, is satisfactory at near optimum temperatures, but is not very satisfactory remote from optimum T. He cites a formulation by Johnson, et al. (1954) which is based upon thermodynamic and physical chemistry precepts and is capable of simulating algal response to temperature over a wide range:

$$k = \frac{CTe^{(-\Delta H^{\ddagger}/RT)}}{1 + e^{(\Delta S/R - \Delta H/RT)}} \tag{3-94}$$

where C = a scaling constant

$\Delta H^{\ddagger}$ = the heat of activation for transition state intermediates

ΔH = the heat of activation for the reaction for which K is the rate coefficient

ΔS = the entropy of activation of the reaction

R = the gas law constant

As Lassiter points out, the thermodynamic constants in Equation (3-94) are difficult to estimate. Lassiter and Kearns (1973) developed a model accounting for the following (quoting Lassiter, 1975):

- "Rate coefficients are always positive, approaching zero asymptotically with respect to values of an external stimulus; thus a change in the rate in response to an external stimulus must be proportional to the magnitude of the rate itself."

- "A biological rate constant reaches maximum at an optimum temperature; therefore, the rate of change of the constant is hypothesized to be proportional to the deviation of temperature from optimum."

- "The rate, which diminishes when the optimum temperature is exceeded (its rate of change becomes negative), decreases more rapidly as the upper limit is approached. An inverse relationship between the rate of change and deviation from the maximum temperature (T_ℓ) is hypothesized."

Based upon these three assumptions, the formulation is given as:

$$\frac{dk}{dT} = \frac{ak^{(T_m - T)}}{(T_\ell - T)} \tag{3-95}$$

Integrating (3-95) with $k = k_m$ when $T = T_m$

$$k = \begin{cases} k_m \left[e^{a(T-T_m)}\right] \left(\frac{T_\ell - T}{T_\ell - T_m}\right)^{a(T_\ell - T_m)} & , T \leq T_\ell \\ \\ 0 & , T > T_\ell \end{cases} \tag{3-96}$$

where a = a scaling constant

k_m = maximal growth rate, day^{-1}

Lassiter notes that the model (Equations (3-95) and (3-96)) has been applied to a number of biological processes including the temperature-dependence of growth rates of Chlorella species, egg production of several wood fungus species, growth rates of four species of aquatic snails, and luminescence from certain luciferin/luciferase reactions. In all cases, using the method of least squares, the fit of the model to the data over a wide range of temperatures has been good.

3.9.2.2.3 Light Levels and the Algal Specific Growth Rate

In addition to the use of a Michaelis-Menton formulation for sub-optimal light levels (discussed in Section 3.9.2.2.1), a number of other formulations to compute the algal specific growth rate as a function of light have been used. Some of the formulations estimate photosynthetic rate, but this can be easily and fairly accurately related to growth rate.

Baca and Arnett (1976) have used a light reduction term developed by Vollenwider as a direct multiplier of $\hat{\mu}$ (the maximal growth rate) as follows:

$$\frac{AI}{\sqrt{1 + (AI)^2}} \cdot \frac{1}{\sqrt{(1 + (\alpha I)^2)^n}} \tag{3-97}$$

where A = low light constant; typically 0.00054

α = photoinhibition factor, lux^{-1}

I = light intensity, lux

n = 1 (from studies by Battelle)

Di Toro, et al. (1971) report that by averaging the expression (over the euphotic depth and over 24 hours):

$$F\,[I(z,t)] = \frac{I(z,t)}{I_s}\, e^{\left[\frac{-I(z,t)}{I_s} + 1\right]} \tag{3-98}$$

the following expression may be obtained:

$$\mu = \hat{\mu}\;\frac{\bar{F}_{max}\, R(t)}{K_r + R(t)} \tag{3-99}$$

where μ = growth rate

I = radiation at depth z at time t

I_s = radiation intensity at which the maximum specific growth rate is achieved (saturation intensity)

z = depth

t = time

$F[I(z,t)]$ = relative photosynthesis

$\bar{F}_{max}$ = maximum fractional reduction in daily specific growth rate over euphotic depth

$R(t)$ = total daily radiation

K_r = total daily radiation at which half of $\bar{F}_{max}$ is attained

The euphotic depth is taken to be the depth to which one percent of the surface radiation penetrates.

Lehman, *et al*. (1975) cite a function for photosynthesis reported by Steele:

$$P(I) = P_{max} \left(I/I_{opt}\right) \exp\left(1-(I/I_{opt})\right) \qquad (3\text{-}100)$$

where P_{max} = maximal photosynthetic rate, any productivity units

$P(I)$ = the photosynthetic rate at light intensity I, units consistent with P_{max}

I = the ambient light intensity, cal cm^{-2} min^{-1}

I_{opt} = light intensity for saturated photosynthetic rate, cal cm^{-2} min^{-1}

Lehman, *et al*. (1975) further modify the expression to account for end-product inhibition:

$$P(I,C) = \left[\left(C_m - C\right)/\left(C_m - C_o\right)\right] P(I) \qquad (3\text{-}101)$$

where C_m = cellular maximum carbon store capacity, mol/cell

C = cellular carbon storage inactive organisms, mol/cell

C_o = cellular growth limiting carbon content, mol/cell

Lassiter (1975) cites a model used by Steele:

$$p = a\ p_m\ I\ e^{1-aI} \qquad (3\text{-}102)$$

where a = a scaling constant

p_m = maximum photosynthetic rate (same variable as P_{max} in Equation (3-100)), productivity units

I = ambient light level, cal cm^{-2} min^{-1}

p = photosynthetic rate at light level I, productivity units

The derivation of the equation was not described by Steele, but Lassiter points out that the formulation fits several sets of photosynthesis-light curves, and suggests a derivation consistent with the following assumptions (quoting Lassiter (1975)):

"1. The rate of change of p with a unit change in I depends both on the value of p and on the deviation of I from the optimum I (I_m);

2. The rate of change of p with a unit change in I is inversely proportional to I, i.e., the photo-inhibition effect."

The formulation is:

$$\frac{dp}{dI} = \frac{k_p \left(1 - I/I_m\right)}{I} \qquad (3\text{-}103)$$

Integrating Equation (3-103),

$$p = p_m \left(I/I_m\right)^k e^{k\left(1-(I/I_m)\right)} \qquad (3\text{-}104)$$

According to Lassiter, Steele had set k = 1 and $1/I_m = a$ to get Equation (3-102).

Substituting the exponential light attenuation equation,

$$I_z = I_o e^{-1.19\eta_T z} \qquad (3\text{-}105)$$

where I_z = light intensity at depth z, cal cm^{-2} min^{-1}

I_o = incident light (at the surface), cal cm^{-2} min^{-1}

η_T = overall extinction rate per meter of depth, accounting for water, color, turbidity

z = depth, m

into Equation (3-102), and integrating over depth (z_e) of the euphotic zone,

$$\overline{p} = p_m \frac{\left(e^{\left[1 - I_o/I_m \, e^{(-1.19 \eta_T z_e)} \right]} - e^{\left(1 - (I_o/I_m) \right)} \right)}{1.19 \eta_T z_e} \qquad (3\text{-}106)$$

where $\overline{p}$ = the average photosynthetic rate over depth

Substituting for p_m an equation attributed to Bannister (Lassiter, 1975),

$$p_m = 12 \, \phi_m \, I_m \, h_c \, C/e \qquad (3\text{-}107)$$

where 12 = the atomic weight of carbon

ϕ_m = maximum quantum yield

C = chlorophyll-a concentration

h_c = the rate of light absorption by chlorophyll-a

and substituting

b = C/B

where B = biomass

b = conversion constant, chlorophyll per unit biomass

into Equation (3-107) and dividing through by B, equation (3-106) becomes:

$$\pi = \frac{12 \, \phi_m \, I_m \, h_c \, b \left(e^{\left[-I_o/I_m \, e^{(-1.19 \eta_T z_e)} \right]} - e^{\left(-I_o/I_m \right)} \right)}{1.19 \eta_T z_e} \qquad (3\text{-}108)$$

where π = the rate of carbon fixation per unit biomass

Then the specific growth rate subject only to light limitation, $\hat{\mu}'$ is given by:

$$\hat{\mu}' = \eta_a \, \pi \qquad (3\text{-}109)$$

where η_a = the stoichiometric coefficient relating total biomass to carbon (fixation)

3.9.2.2.4 Michaelis-Menton Constants - Deficiencies of the Approach

One of the commonly used formulations for correcting $\hat{\mu}$ (saturated growth rate) for limiting nutrients and suboptimal light is the Michaelis-Menton expression (see Section 3.9.2.2.1). The theory is based upon the work of Michaelis and Menton in 1913 and of Monod (see Sykes, 1973), and was originally applied to enzyme kinetics. Monod applied it to continuously stirred chemostat cultures.

In order to relate the ambient concentration of some limiting nutrient, S, to the growth rate, μ, Monod proposed a relationship of the form

$$\mu = \hat{\mu} \frac{S}{K + S} \qquad (3\text{-}110)$$

where μ = specific growth rate, day^{-1}

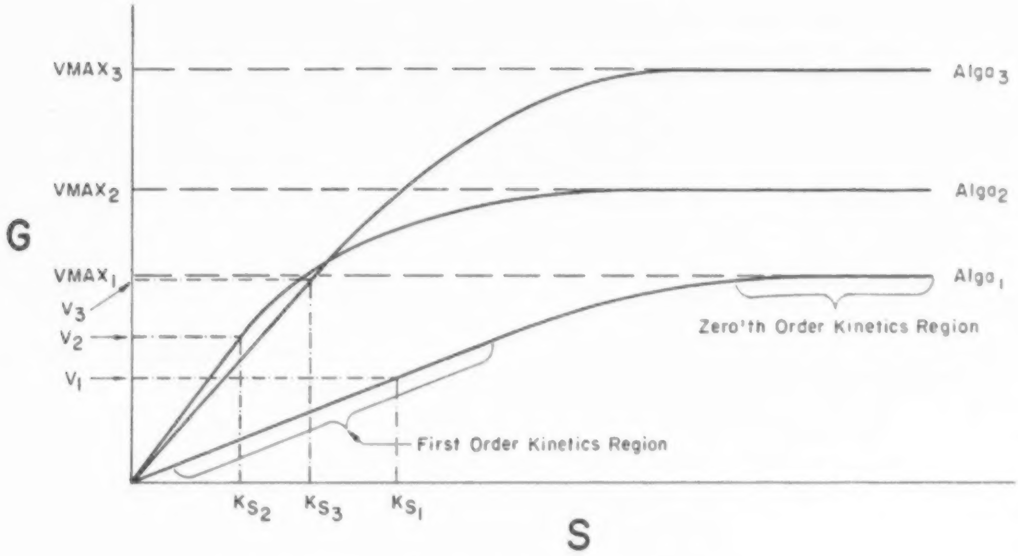
$\hat{\mu}$ = maximum specific growth rate, day^{-1}

K = a constant, same units as S

This is the form widely adopted and used in many models which simulate algal population dynamics. Equations (3-73), (3-74), (3-75), and (3-78) all incorporate this formulation.

The constant K in Equation (3-110) is called the Michaelis-Menton half-saturation constant. The form of Equation (3-110) is hyperbolic, and is as shown in Figure 3-13, which represents the responses of three different algae to changes in concentration of a hypothetical factor, S. The plot also shows the significance of K, the half-saturation constant, and order of growth kinetics.

The Michaelis-Menton formulation has several problems when used as in Equation (3-74). First, the application implicitly assumes that the effect of several suboptimal factors is simply multiplicative, although there is certainly no compelling reason to assume such a relationship. Equation (3-76) goes to the other extreme, assuming that only one nutrient can be limiting. This is known to be untrue. Furthermore, none of the expressions presented earlier account for luxury uptake. Luxury uptake occurs under circumstances where there is an excess of a particular nutrient. The nutrient is then stored and used when there is a deficiency of that nutrient. This phenomenon is likely to result in the Michaelis-Menton formulation overestimating the impact of short-term, transient nutrient deficiencies, and a lag in long-term deficiency impacts being manifested physically in the prototype.



VMAX represents the maximum growth rate (G) for each algal species. K_S is the substrate concentration (S) at which the growth rate is half maximal (V). Within the region labeled "first order kinetics," the growth rate is a function of S and might be represented as $dC/dt = kS$ while in the zero'th order kinetics region, the growth rate is independent of substrate concentration. Here, other factors limit G.

Figure 3-13. Growth kinetics of three hypothetical algal species as a function of substrate concentration.

In a discussion by Mar (1976), the very use of the Monod theory is brought into question. Mar cites observed variations in values for the half-saturation constants, suggesting that the variability may be due more to an improper formulation in the Monod theory than to true variability of algal nutrient requirements. If the change in biomass per unit time is given as:

$$\frac{dB}{dt} = \mu_s \left(\frac{S}{K_s + S} \right) B, \tag{3-111}$$

where B = biomass concentration

K_s = Michaelis-Menton half-saturation constant

S = substrate concentration

Mar points out that under conditions of large S, greater biomass concentrations result in greater productivity predictions (reasonable). However, where S becomes very small, Equation (3-111) approaches:

$$\frac{dB}{dt} = \mu_s \left(\frac{S}{K_s} \right) B \qquad (3\text{-}112)$$

which states that an increase in biomass will still result in increased productivity. In fact, regardless of how small S becomes, and how clearly limiting the substrate represented actually is in the prototype, if B is very large, the model will predict substantial increases in biomass. Mar points out, further, that the introduction of a decay term into the expression as:

$$\frac{dB}{dt} = \mu_s \left(\frac{S}{K_s + S} \right) B - K_d B \qquad (3\text{-}113)$$

or

$$\frac{dB}{dt} = \left[\mu_s \left(\frac{S}{K_s + S} \right) - K_d \right] B \qquad (3\text{-}114)$$

where K_d = decay rate

does not solve the problem since under the condition:

$$1 \gg \left(\mu_s \left(\frac{S}{K_s + S} \right) - K_d \right) > 0,$$

the same anomalous growth dependence upon biomass is described. That is, for constant and small S, productivity is a function of biomass.

Mar has suggested an alternative expression which does not depend upon Michaelis-Menton half-saturation constants. The expression is of the same form as the Monod formulation:

$$\mu = \mu_s \left(\frac{\alpha S}{B + \alpha S} \right) \qquad (3\text{-}115)$$

where α = conversion of substrate to biomass.

It should be noted that as S becomes small, and

$$\mu \simeq \mu_s \alpha S/B, \tag{3-116}$$

$$\frac{dB}{dt} \simeq B\mu_s \ \alpha S/B = \mu_s \ \alpha S \tag{3-117}$$

Thus for small S, productivity is not materially affected by the value of B.

3.9.2.2.5 Half-Saturation Constant Values

Table 3-34 lists reported values of the half-saturation constants for nitrogen, phosphorus, silicate, carbon, and light. Other data are also presented in the table including saturated growth rates and saturated light intensities. Table 3-35 presents Michaelis-Menton half-saturation constants as reported by Di Toro, et al. (1971). Table 3-36, taken from Eppley, et al. (1969), provides nitrogen half-saturation constants for marine phytoplankton, while Table 3-37 provides values from Lehman, et al. (1975). Table 3-38 shows minimum cell nutrient quotas for some marine and freshwater phytoplankton.

3.9.2.2.6 Temperature Correction Constants

A commonly used temperature correction formulation for algal growth rates is given above as Equation (3-85). The same formulation was cited in Equation (3-72). The expression for the algal specific growth rate is:

$$\mu = \hat{\mu}\theta^{(T-T_r)} \tag{3-118}$$

Values of θ are presented in Table 3-39 (from Di Toro, 1971).

3.9.3 Phytoplankton Specific Death Rate, D_p

3.9.3.1 Factors Affecting D_p

The algal specific death rate, D_p in Equation (3-70) represents all sinks of phytoplankton biomass. Sinks include the endogenous respiration rate, grazing by zooplankton and other herbivores, settling, parasitization, and stress-induced death.

3.9.3.1.1 Endogenous Respiration Rate

The endogenous respiration rate is the time rate of algal biomass conversion back to carbon dioxide per unit weight of organic carbon content (O'Connor, et al., 1973). As a process, it can be considered as the inverse of photosynthesis. Endogenous respiration, while providing for the maintenance of the algal cell and its direct energy requirements, may be considered as partial death of the cell since biomass is consumed.

TABLE 3-34. VALUES FOR THE HALF-SATURATION CONSTANT IN MICHAELIS-MENTON GROWTH FORMULATIONS

Phytoplankton Description	Maximum Specific Growth Rate,(Days^{-1})	HALF-SATURATION CONSTANTS					Reference
		Nitrogen (mg/l)	Phosphorus (mg/l)	Silicate (mg/l)	Carbon (mg/l)	Light (Kcal/m^2/sec)	
Total Phytoplankton	0.2-8.0	0.025-0.3	0.006-0.03	-	-	-	Baca and Arnett (1976)
Total Phytoplankton	2.0	0.025	-	-	-	-	O'Connor, et al. (1975)
Total Phytoplankton	2.5	0.025	-	-	-	-	O'Connor, et al. (1975)
Total Phytoplankton	2.0	0.025	0.005	-	-	-	O'Connor, et al. (1975)
Total Phytoplankton	1.3	0.025	0.010	-	-	-	O'Connor, et al. (1975)
Total Phytoplankton	2.1	0.025	0.002	-	-	-	O'Connor, et al. (1975)
Total Phytoplankton	1.0-2.0	0.025	0.006-0.025	-	-	-	Battelle (1974)
Warm Water	2.0	0.07	0.015	-	0.03	0.002	Tetra Tech (1976)
Warm Water	1.-2	0.05-0.3	0.02-0.05	-	0.[illegible]-0.6	0.002-0.004	U.S. Army Corps of Engineers (1974)
Cold Water	2.5	0.01	0.02	-	0.04	0.003	Tetra Tech (1976)
Cold Water	1.-3.	0.1-0.4	0.004-0.0[illegible]	-	0.5-0.8	0.004-0.006	U.S. Army Corps of Engineers (1974)
Diatoms	2.1 (25°C)	-	-	-	-	-	Bierman (1976)
Small Diatoms	2.1	-	-	0.03	-	-	Canale, et al. (1976)
Large Diatoms	2.0	-	-	0.03	-	-	Canale, et al. (1976)
Green	1.9 (25°C)	-	-	-	-	-	Bierman (1976)
Green	1.9	0.015	0.0025	-	-	-	Canale, et al. (1976)
Blue-Green	1.6	0.015	0.0025	-	-	-	Canale, et al. (1976)
Blue-Green (N-Fixing)	0.8 (25°C)	-	-	-	-	-	Bierman (1976)
Blue-Green (Non N-Fixing)	0.8 (25°C)	-	-	-	-	-	Bierman (1976)
Small Cells Favoring Low Nutrients	1.0	0.3	0.03	-	0.5	0.003	Chen and Orlob (1975)
Small Cells Favoring Low Nutrients	1.5	0.3	0.03	-	0.5	0.002	Chen (1970)
Large Cells Favoring High Nutrients	2.0	0.4	0.05	-	0.6	0.006	Chen and Orlob (1975)
Large Cells Favoring High Nutrients	2.0	0.4	0.05	-	0.6	0.004	Chen (1970)
Readily Grazed Fast Settling	1.5	0.02	0.02	-	0.05	0.003	Chen and Wells (1975)
Not Readily Grazed Not Fast Settling	2.0	0.4	0.05	-	0.8	0.006	Chen and Wells (1975)

(continued)

TABLE 3-34 (continued)

Phytoplankton Description	Saturated Light Intensity (Ft-Candles)	Chemical Composition (fraction by weight) C	N	P	Temperature Tolerance Limits (°C)	Location of Study	Reference
Total Phytoplankton	-	-	-	-	-	-	Baca and Arnett (1976)
Total Phytoplankton	300	-	-	-	-	San Joaquin River	O'Connor, *et al*. (1975)
Total Phytoplankton	300	-	-	-	-	San Joaquin Delta Estuary	O'Connor, *et al*. (1975)
Total Phytoplankton	300	-	-	-	-	Potomac Estuary	O'Connor, *et al*. (1975)
Total Phytoplankton	350	-	-	-	-	Lake Erie	O'Connor, *et al*. (1975)
Total Phytoplankton	350	-	-	-	-	Lake Ontario	O'Connor, *et al*. (1975)
Total Phytoplankton	-	-	-	-	-	Grays Harbor/Chehalis River, Washington	Battelle (1974)
Warm Water	-	0.4	0.08	0.015	10-30	N. Fork Kings River, Calif.	Tetra Tech (1976)
Warm Water	-	-	-	-	10-30	-	U.S. Army Corps of Engineers (1974)
Cold Water	-	0.4	0.08	0.015	5-25	N. Fork Kings River, Calif.	Tetra Tech (1976)
Cold Water	-	-	-	-	5-25	-	U.S. Army Corps of Engineers (1974)
Diatoms	-	-	-	-	-	Saginaw Bay, Lake Huron	Bierman (1976)
Small Diatoms	-	-	-	-	-	Lake Michigan	Canale, *et al*. (1976)
Large Diatoms	-	-	-	-	-	Lake Michigan	Canale, *et al*. (1976)
Green	-	-	-	-	-	Saginaw Bay, Lake Huron	Bierman (1976)
Green	-	-	-	-	-	Lake Michigan	Canale, *et al*. (1976)
Blue-Green	-	-	-	-	-	Lake Michigan	Canale, *et al*. (1976)
Blue-Green (N-fixing)	-	-	-	-	-	Saginaw Bay, Lake Huron	Bierman (1976)
Blue-Green (Non N-Fixing)	-	-	-	-	-	Saginaw Bay, Lake Huron	Bierman (1976)
Small Cells Favoring Low Nutrients	-	-	-	-	-	Lake Washington	Chen and Orlob (1975)
Small Cells Favoring Low Nutrients	-	-	-	-	-	San Francisco Bay Estuary	Chen (1970)
Large Cells Favoring High Nutrients	-	-	-	-	-	Lake Washington	Chen and Orlob (1975)
Large Cells Favoring High Nutrients	-	-	-	-	-	San Francisco Bay Estuary	Chen (1970)
Readily Grazed Fast Settling	-	0.5	0.09	0.015	-	Boise River, Idaho	Chen and Wells (1975)
Not Readily Grazed Not Fast Settling	-	0.5	0.09	0.015	-	Boise River, Idaho	Chen and Wells (1975)

TABLE 3-35. MICHAELIS-MENTON HALF-SATURATION CONSTANTS FOR NITROGEN AND PHOSPHORUS (FROM DI TORO, ET AL., 1971)

Organism	Nutrient	Michaelis Constant, μg/Liter as N or P
Chaetoceros gracilis (marine diatom)	PO_4	25
Scenedesmus gracile	Total N	150
	Total P	10
Natural association	PO_4	6[a]
Microcystis aeruginosa (blue-green)	PO_4	10[a]
Phaeodactylum tricornutum	PO_4	10
Oceanic species	NO_3	1.4-7.0
Oceanic species	NH_3	1.4-5.6
Neritic diatoms	NO_3	6.3-28
Neritic diatoms	NH_3	7.0-120
Neritic or littoral	NO_3	8.4-130
Flagellates	NH_3	7.0-77
Natural association	NO_3	2.8
Oligotrophic	NH_3	1.4-8.4
Natural association	NO_3	14
Eutrophic	NH_3	18

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[a] Estimated.

TABLE 3-36. MICHAELIS-MENTON HALF-SATURATION CONSTANTS (K_S) FOR UPTAKE OF NITRATE AND AMMONIUM BY CULTURED MARINE PHYTOPLANKTON AT 18°C. K_S UNITS ARE μMOLES/LITER (AFTER EPPLEY, *ET AL*., 1969)

Organism	NITRATE		AMMONIUM		Cell Diam[*] (μ)
	K_s	±95% Conf. Limit	K_s	±95% Conf. Limit	
Oceanic species					
Coccolithus huxleyi BT-6	0.1	0.3[†]	0.1	0.7	5
C. huxleyi F-5	0.1	1.6	0.2	0.9	5
Chaetoceros gracilis	0.3,0.1	0.5,0.2	0.5,0.3	0.5,0.3	5
Cyclotella nana 13-1	0.3,0.7	0.4,0.5	0.4	0.3	5
Neritic diatoms					
Skeletonema costatum[‡]	0.5,0.4	0.4,0.1	3.6,0.8,0.8	0.8,0.7,0.5	8
Leptocylindrus danicus	1.3,1.2	0.5,0.1	3.4,0.9,0.5	1.4,0.2,0.4	21
Rhizosolenia stolterfothii	1.7	0.4	0.5,0.5	0.9,0.4	20
R. robusta[§]	3.5,2.5	1.0,1.0	5.6,9.3	2.0,1.5	85
Ditylum brightwellii	0.6	1.7	1.1	0.6	30
Coscinodiscus lineatus	2.4,2.8	0.5,0.6	2.8,1.2	2.6,1.0	50
C. wailesii	2.1,5.1	0.3,1.8	4.3,5.5	5.4,2.0	210
Asterionella japonica	0.7,1.3	0.3,0.5	1.5,0.6	1.2,0.8	10
Neritic or littoral flagellates					
Gonyaulax polyedra	8.6,10.3	---,2.4	5.7,5.3	0.6,1.1	45
Gymnodinium splendens	3.8	0.9	1.1	1.0	47
Monochrysis lutheri	0.6	0.3	0.5	0.4	5
Isochrysis galbana	0.1,0.1	0.2,0.2	--	--	5
Dunaliella tertiolecta	1.4	1.1	0.1	0.6	8
Natural marine communities (from MacIsaac and Dugdale, 1969)					
Oligotrophic	≤0.2(6 expts)		0.1-0.6(3 expts)		
Eutrophic	≥1.0(3 expts)		1.3 (1 expt)		

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[*] Geometric mean diameter rounded off to the nearest micron.

[†] This notation means that $-0.2 < K_S < 0.4$. Negative K_S values have no physical interpretations.

[‡] At 28°C, K_S for nitrate uptake was 1.0 ± 0.5; at 8°C, it was 0.0 ± 0.5.

[§] An oceanic species according to Cupp (1943).

TABLE 3-37. HALF-SATURATION CONSTANTS FOR N, P, AND Si UPTAKE (μM) REPORTED FOR MARINE AND FRESHWATER PLANKTON ALGAE (AFTER LEHMAN, *ET AL*., 1975)

Cyclotella nana	NO_3	0.4-1.9	Carpenter and Guillard (1971)
		1.8	MacIsaac and Dugdale (1969)
		0.35	Caperon and Meyer (1972)
		0.5	Eppley, *et al*. (1969)
	NH_4	0.4	
Dunaliella tertiolecta	NO_3	0.21	Caperon and Meyer (1972)
	NH_4	0.17	
	NO_3	1.4	Eppley, *et al*. (1969)
	NH_4	0.6	
Asterionella japonica	NO_3	0.7-1.3	Eppley and Thomas (1969)
		1.0	Eppley, *et al*. (1969)
	NH_4	1.0	
Monochrysis lutheri	NO_3	0.42	Caperon and Meyer (1972)
	NH_4	0.29	
	NO_3	0.6	Eppley, *et al*. (1969)
	NH_4	0.4	
Fragilaria pinnata	NO_3	0.6-1.6	Carpenter and Guillard (1971)
Bellochia sp.	NO_3	0.1-0.9	
Coccochloris stagnina	NO_3	0.31	Caperon and Meyer (1972)
Phaeodactylum tricornutum	NO_3	2.6	Ketchum (1939)
Anabaena cylindrica	NO_3	70.	Hattori (1962)
	NO_2	40.	
Chlorella pyrenoidosa	NO_2	25.	Knudsen (1965)
Chaetoceros gracilis	NO_3	0.2	Eppley, *et al*. (1969)
	NH_4	0.4	
Gonyaulax polyedra	NO_3	9.5	
	NH_4	5.5	
Gymnodinium splendens	NO_3	3.8	
	NH_4	1.1	
Coccolithus huxleyi	NO_3	0.1	
	NH_4	0.1	
Skeletonema costatum	NO_3	0.45	
	NH_4	0.8	
Isochrysis galbana	NO_3	0.1	
Leptocylindricus danicus	NO_3	1.25	Eppley, Rogers and McCarthy (1969)
	NH_4	0.7	
Rhizosolenia stolterfothii	NO_3	1.7	
	NH_4	0.5	
Rhizosolenia robusta	NO_3	3.0	
	NH_4	7.5	
Ditylum brightwellii	NO_3	0.6	
	NH_4	1.1	
Coscinodiscus lineatus	NO_3	2.6	
	NH_4	2.0	
Coscinodiscus wailesii	NO_3	3.6	
	NH_4	4.9	
Euglena gracilis	PO_4	16.	Blum (1966)
Cyclotella nana	PO_4	0.58	Fuhs, *et al*. (1972)
Thalassiosira fluviatilis	PO_4	1.72	
Chlorella pyrenoidosa	PO_4	4.-5.	Jeanjean (1969)
Nitzschia actinastreoides	PO_4	1.0	Müller (1972)
Scenedesmus sp.	PO_4	0.6	Rhee (1973)
Pediastrum duplex	PO_4	1.1	Lehman unpublished
Dinobryon cylindricum	PO_4	0.8	
D. sociale var. *americanum*	PO_4	0.5	
Nitaschia actinastreoides	Si	3.5	Muller (1972)
Thalassiosira pseudonana	Si	1.4-2.9	Paasche (1973a)
	Si	1.39	Paasche (1973b)
Thalassiosira decipiens	Si	3.37	
Skeletonema costatum	Si	0.80	
Licmophora sp.	Si	2.58	
Ditylum brightwellii	Si	2.96	

TABLE 3-38. MINIMUM CELL NUTRIENT QUOTAS (μMOLES CELL^{-1}) OF P, Si, AND N FOR SOME MARINE AND FRESHWATER PHYTOPLANKTON (AFTER LEHMAN, *ET AL*., 1975)

Phosphorus:		
Asterionella formosa	2×10^{-9} $1.5\text{-}3. \times 10^{-9}$	Mackereth (1953) Müller (1972)
Asterionella japonica	1.5×10^{-9}	
Cyclotella nana	0.9×10^{-9}	Fuhs (1969)
Nitzschia actinastreoides	3×10^{-9} (35μ)** 4×10^{-9} (50-55μ)**	Muller (1972)
Phaeodactylum tricornutum	2×10^{-9}	
Chlorella pyrenoidosa	3×10^{-9}	
Scenedesmus quadricauda	4.5×10^{-9}	
Scenedesmus sp.	1.7×10^{-9}	Rhee (1973)
Thalassiosira fluviatilis	12.5×10^{-9}	Fuhs, *et al*. (1972)
A. formosa	3×10^{-8}	Grim (1939)*
Gymnodinium	1.1×10^{-8}	
Dinobryon	0.5×10^{-9}	
Anabaena	2.5×10^{-9}	
Silicon:		
Navicula pelliculosa	0.5×10^{-7}	Busby and Lewin (1967)
Nitzschia alba	3×10^{-7}	Lewin and Chen (1968)
Asterionella formosa	2×10^{-6} 1.8×10^{-6}	Hughes and Lund (1962) Grim (1939)*
Fragilaria crotonensis	4×10^{-6}	
Thalassiosira pseudonana	2×10^{-8}	Paasche (1973a)
Nitrogen:		
Isochrysis galbana	3×10^{-8}	Droop (1973)
Asterionella formosa	6×10^{-7}	Grim (1939)*
Gymnodinium	3.9×10^{-7}	
Dinobryon	1.8×10^{-8}	
Anabaena	1×10^{-7}	

*These quantities are not necessarily the minimum.

**Cell length.

TABLE 3-39. MAXIMUM (SATURATED) GROWTH RATES AS A FUNCTION OF TEMPERATURE (FROM DI TORO, ET AL., 1971)

Organism	Temperature	Saturated Growth Rate, K' Base e, Day^{-1}
Chlorella ellipsoidea	25	3.14
(green alga)	15	1.2
Nannochloris atomus	20	2.16
(marine flagellate)	10	1.54
Nitzschia closterium	27	1.75
(marine diatom)	19	1.55
	15.5	1.19
	10	0.67
Natural association	4	0.63
	2.6	0.51
Chlorella pyrenoidosa	25	1.96
Scenedesmus quadricauda	25	2.02
Chlorella pyrenoidosa	25	2.15
Chlorella vulgaris	25	1.8
Scenedesmus obliquus	25	1.52
Chlamydomonas reinhardti	25	2.64
Chlorella pyrenoidosa	10	0.2
(synchronized culture)	15	1.1
(high-temperature strain)	20	2.4

According to O'Connor, et al. (1973), the temperature dependence of endogenous respiration has been investigated, and a straight line fit seems reasonable. Lund (1965) has noted that under nutrient depletion, some algae go into a kind of morphological or physiological resting stage. O'Connor, et al. suggest that, whereas endogenous respiration is nutrient dependent, in some cases an expression such as the Michaelis-Menton formulation might be useful for simulating endogenous respiration.

3.9.3.1.2 Grazing

Herbivorous zooplankton reduce water column phytoplankton through grazing. According to O'Connor, et al.(1973), the interaction between phytoplankton and herbivorous zooplankton is quite complex, and only a first approximation to the process can be given. Herbivorous zooplankton feed by straining the water and removing whatever phytoplankton and detritus are present. The phytoplankton represent a food source for the zooplankton, and phytoplankton blooms are commonly associated with succeeding blooms of herbivorous zooplankton.

The zooplankton grazing rate, according to O'Connor, et al., is commonly expressed in terms of volume of water filtered per unit of zooplankton biomass per unit time. This representation, of course, is very convenient from a simulation standpoint. The filtering rate of herbivorous zooplankton has been observed to vary with temperature, the degree of variation being zooplankton species dependent. O'Connor, et al. note that the filtering rate is also dependent upon particulate concentration (Burns and Rigler, 1967), phytoplankton cell size (Mullin, 1963), and concentration of phytoplankton (McMahon and Rigler, 1965). Further, selective grazing according to phytoplankton cell size has also been observed (Burns, 1969).

3.9.3.1.3 Settling, Parasitization, and Stress

Settling out of phytoplankton is known to involve a complex set of phenomena including vertical turbulence effects, vertical density distribution, and the physiological state of the different species of phytoplankton (Thomann, et al., 1975). With regard to species, the generation of gelatinous sheaths by phytoplankton, for example, has been shown to be of importance in settling, and apparently the settling velocity of nutrient rich cells is somewhat lower than that of cells that are nutritionally deficient. In some instances the phytoplankton settling velocity may be zero or the cells may be sufficiently buoyant to move upward in the water column (Thomann, et al., 1975). Thomann, et al. (1975) report on work by Burns and Pashley which shows a general decrease in settling velocity with depth and a marked seasonal variation of settling velocity.

Lombardo (1972) reports on work done by Eppley, et al. which suggests that there are three discrete levels of phytoplankton sinking rates. These may be differentiated as follows:

1. rate during logarithmic growth

2. rate during the stationary period

3. rate found in neutrally buoyant cells

In those rivers and estuaries where the primary transport is one-dimensional along the longitudinal axis of flow, settling may not be significant. The mixing and turbulence associated with both freshwater flow and tidal action are frequently of sufficient magnitude to minimize settling effects (O'Connor, et al., 1975).

Parasitization and stress are two other factors which may contribute to the death of algal cells. Parasitization represents the infection of the algal cell by other microorganisms. Stress can result from nonoptimal conditions (distinct from changes in growth rates) and from the presence of toxic substances, although the modeling of toxic substances is commonly done by altering the respiration or growth rate. In reality, of course, toxic substances might well affect any or all of the rates of respiration, growth, settling, and death.

3.9.3.2 Modeling the Phytoplankton Specific Death Rate

Di Toro, et al. (1971), O'Connor, et al. (1975), Thomann, et al. (1975), and the Fisheries Research Board of Canada (Simons, 1976) have proposed a general expression describing the phytoplankton death rate of the following type:

$$D_p = K_2 + C_g Z \left(\frac{K_{mp}}{K_{mp} + P} \right) - \frac{W}{H} \qquad (3\text{-}119)$$

where K_2 = endogenous respiration rate of phytoplankton, a function of temperature, day^{-1}

C_g = grazing rate of herbivorous zooplankton, 1/day-mg zooplankton carbon

Z = zooplankton carbon concentration, mg/l

K_{mp} = Michaelis-Menton half-saturation constant for zooplankton grazing on phytoplankton, mg/l

W = settling velocity, m/day

P = phytoplankton concentration, mg/l

H = depth for settling out, m

The same investigators and others (Thomann, et al., 1974; and Lombardo, 1973; in modeling studies of the Potomac and San Joaquin Delta Estuaries), represented the temperature corrected endogenous respiration rate, R (in

day^{-1}), as a linear function of temperature as follows:

$$R = K_2\ T \qquad (3\text{-}120)$$

where K_2 = endogenous respiration rate, $\text{day}^{-1}\,{}^\circ\text{C}^{-1}$

T = temperature, °C

In a modeling study for Lake Ontario, Thomann, et al. (1975), proposed the following expression for endogenous respiration:

$$R = K_2\ \theta^{(T-20)} \qquad (3\text{-}121)$$

where K_2 = endogenous respiration rate, day^{-1}

θ = temperature coefficient; typically 1.08

As discussed earlier, the filtering rate, C_g, in formulations like Equation (3-119) is known to vary as a function of the size of the phytoplankton cell being ingested, the concentration of the phytoplankton, the amount of particulate matter present, and temperature. However, as an approximation, a single constant grazing coefficient, C_g, is used.

Baca and Arnett (1976) used the following representation for the phytoplankton death rate (day^{-1}) in their water quality model:

$$D_p = F_1 + F_2 \qquad (3\text{-}122)$$

where F_1 = algal respiration rate, day^{-1}

F_2 = algal decomposition rate, day^{-1}; typically 0.003-0.17

Tetra Tech (1975, 1976) and the U.S. Army Corps of Engineers (1974) consider the phytoplankton death rate, D_p, to be a function of endogenous respiration, zooplankton grazing, and sinking losses. Generally, two values of respiration are available in their formulations. When the temperature is below the lower bound of a temperature tolerance limit, the standard respiration rate is used; otherwise the active respiration rate is used. Tetra Tech (1975, 1976) and Chen and Wells (1975) consider the amount of phytoplankton biomass consumed by the zooplankton to be a function of both the amount of algae grazed and the digestive efficiency of the zooplankton.

A formulation used by Bierman (1976) for the phytoplankton death rate, D_p, also considers losses to be due to respiration (and cell death), grazing, and sinking. His death term is formulated as follows:

$$R = \text{RLYS} \cdot T \cdot \text{TCROP} \qquad (3\text{-}123)$$

where R = rate of phytoplankton biomass loss, day^{-1}

RLYS = algal death rate $(\text{day-°C-mg/l})^{-1}$

T = temperature, °C

TCROP = total phytoplankton biomass, mg/l

Lombardo (1972) reports an expression for the phytoplankton death rate which is essentially the same as that given by Thomann, O'Connor and Di Toro. Lehman (1975) considers the algal specific death rate to be due to respiration and physiological mortality. The formulation for the loss of algal cells due to algal death is

$$\frac{dN}{dt} = \left[.693\,\mu - (V/D) - M \right] N \qquad (3\text{-}124)$$

and

$$M = M_{max} \left[1 - \exp(k \cdot SG) \right] \qquad (3\text{-}125)$$

where N = algal cell concentration, numbers/ml

μ = cell division rate, day^{-1}

V = sinking rate, m/day

D = mean epilimnetic depth, m

M = fraction of population dying per day

M_{max} = maximal fraction dying per day at suboptimal condition

SG = number of suboptimal days

k = .693/d

d = number of suboptimal days required for $M = M_{max}/2$

Lassiter (1975) uses the formulation:

$$D_T = \begin{cases} -a \ln k/k_m & , T \geq T_m \\ 0 & T < T_m \end{cases} \qquad (3\text{-}126)$$

where D = the specific death rate due to excessive temperature, day^{-1}

T = ambient temperature, °C

T_m = optimal temperature, °C

a = scaling coefficient, day^{-1}

k = k in Equation (3-96), day^{-1}

k_m = k_m in Equation (3-96), day^{-1}

3.9.3.3 Values for Algal Specific Death Rates and Related Constants

Table 3-40 provides rate values for algal respiration, zooplankton filtering, and algal sinking, and values of the Michaelis grazing constant and zooplankton digestive efficiency. Values given are for 20°C unless noted otherwise. Tables 3-41 and 3-42 are from Di Toro, et al. (1971) and show rates of phytoplankton endogenous respiration and zooplankton grazing rates.

3.9.4 Benthic Algae

Through photosynthesis, benthic algae and rooted aquatic plants affect some of the major water quality parameters, e.g., dissolved oxygen and nutrient concentrations. In a stream, benthic algae and rooted aquatic plants can be a major influence on the dissolved oxygen resources due to photosynthetic processes taking place during the day and respiration processes occurring at night. Benthic algae and rooted aquatic plants also may influence the nutrient content of flowing water by their extraction of nutrients. A stream which supports benthic algae may exhibit a decrease in eutrophying influence on a receiving lake by the fixing of organic nutrients in the stream and resulting reduction in nutrient discharge.

Benthic algal dynamics, when considered in a water quality model, are usually treated in the same way as phytoplankton dynamics, except that benthic algae are stationary within a reach and are not allowed to exceed a maximum concentration (Lombardo, 1972; Lombardo, 1973).

3.9.5 Methods for Measuring Algal Growth and Death Rates and Coefficients

Methods for measuring the various rates and coefficients described above are generally much too complex and organism-specific to discuss here. The reader is referred to the substantial body of technical literature on the various specific subjects. Table 3-43 provides references on various topics which may be helpful in initiating a literature review on parameters discussed in this section.

TABLE 3-40. VALUES FOR COEFFICIENTS IN PHYTOPLANKTON SPECIFIC DEATH RATE EXPRESSIONS

Phytoplankton Description	Algal Respiration Rate @20°C (day^{-1})	Zooplankton Filtering Rate @20°C (1/mg-C-day)	Zooplankton Digestive Efficiency (mg/mg)	Sinking Rate (m/day)	Michaelis Grazing Constant (μg chlor/1)	Location of Study	Reference
Phytoplankton	0.005-0.12	-	-	-	-	-	Baca and Arnett (1976)
Phytoplankton	-	-	0.5-0.8	0.-2.	-	Lake Washington	Chen and Orlob (1975)
Phytoplankton	0.08	-	-	0.00-0.005	-	Lake Michigan	Canale, et al. (1976)
Phytoplankton	0.10	0.13	0.6	-	50	San Joaquin River	O'Connor, et al. (1975)
Phytoplankton	0.08	0.25	0.65	-	50	Lake Erie	O'Connor, et al. (1975)
Phytoplankton	0.10	1.2	0.60	0.1	10	Lake Ontario	O'Connor, et al. (1975)
Phytoplankton	0.10	0.18	0.60	-	50	San Joaquin Delta Estuary	O'Connor, et al. (1975)
Phytoplankton	0.10	-	-	-	-	Potomac Estuary	O'Connor, et al. (1975)
Phytoplankton	0.10	-	-	0.4	-	-	Lombardo (1972)
Phytoplankton	0.10±0.02	0.13	-	-	-	-	Di Toro, et al. (1971)
Phytoplankton	0.1	-	-	0.5	-	Boise River, Idaho	Chen and Walls (1975)
Phytoplankton	-	-	-	0.5	-	San Francisco Bay Estuary	Chen (1970)
Warm Water	0.1 (active) 0.01 (inactive)	-	0.7	0.2	-	N. Fork Kings River, California	Tetra Tech (1976)
Warm Water	0.05	-	-	0.2	-	Lake Washington	Chen and Orlob (1975)
Cold Water	0.1 (active) 0.01 (inactive)	-	0.7	0.05	-	N. Fork Kings River, California	Tetra Tech (1976)
Cold Water	0.05	-	-	0.05	-	Lake Washington	Chen and Orlob (1975)
Diatoms/Greens	0.0015*	0.35-0.50**	-	0.4	-	Saginaw Bay, Lake Huron	Bierman (1976)
Blue-Greens	0.0015*	0.35-0.50**	-	0.15	-	Saginaw Bay, Lake Huron	Bierman (1976)

* - 0.0015 (day-°C-mg/1)$^{-1}$

** - 0.35-0.50 mg algae/mg zooplankton -day

TABLE 3-41. VALUES FOR ENDOGENOUS RESPIRATION RATES OF PHYTOPLANKTON (DI TORO, *ET AL.*, 1971)

Organism	Temper-ature, °C	Endogenous Respiration Rate, Day^{-1} (Base$_e$)
Nitzschia closterium	6	0.035
	35	0.170
Nitzschia closterium	20	0.08
Coscinodiscus excentricus	16	0.075
	16	0.11
Natural association	2	0.03
	18	0.12
	2.0	0.024±0.012
	17.9	0.110±0.007

TABLE 3-42. VALUES FOR GRAZING RATES OF ZOOPLANKTON (DI TORO, *ET AL.*, 1971)

Organism	Reported Grazing Rate	Grazing Rate, Liter/Mg Dry Wt.-Day
Rotifer		
Brachionus calyciflorus	0.05-0.12[a]	0.6-1.5
Copepod		
Calanus sp.	67-208[b]	0.67-2.0
Calanus finmarchicus	27[a]	0.05
Rhincalanus nasutus	98-670[a]	0.3-2.2
Centropages hamatus		0.67-1.6
Cladocera		
Daphnia sp.		1.06
Daphnia sp.		0.2-1.6
Daphnia magna	81[a]	0.74
Daphnia magna	57-32[a]	0.2-0.3
Natural association		
Georges Bank	80-110[b]	0.8-1.10

[a] ml/animal-day

[b] ml/mg wet wt-day

TABLE 3-43. REFERENCES FOR METHODS OF MEASUREMENT OF VARIOUS ALGAL MODELING PARAMETERS

Reference	Subject
Braarud (1961)	Cultivation of organisms
Cassie (1963)	Multivariate analysis of phytoplankton data
Eppley, et al. (1966)	Marine phytoplankter culture
Eppley (1968)	Carbon content of phytoplankton
Eppley, et al. (1969)	Half-saturation constants
Fitzgerald and Nelson (1966)	Limiting and surplus phosphorus in algae
James and Birge (1938)	Light absorption
Megard (1972)	Rates of photosynthesis and phytoplankton growth
Powers, et al. (1972)	Nutrient limitation of algae
Smayda (1969b)	Settling of algae
Strickland (1960)	Marine phytoplankton production

3.9.6 Summary

Phytoplankton can dramatically affect surface water quality through photosynthesis, respiration, nutrient uptake, and death. In general, modeling approaches consider rates of growth (a source of phytoplankton biomass) and respiration, settling, and zooplankton grazing (sinks of phytoplankton biomass). Factors influencing the growth rate are phytoplankton type, nutrient availability, light intensity and duration, and temperature. The impacts of nutrient and light growth limitation are generally modeled using a Monod or Michaelis-Menton type formulation, although this has a number of deficiencies.

Factors affecting the death rate include phytoplankton species, abundance of predators, temperature, presence of toxic substances, and osmotic conditions. Respiration, which may be conceptualized as the inverse of photosynthesis, consumes biomass carbon and is simulated as one component of death. Toxic substance effects are sometimes simulated as growth-limiting factors rather than as factors affecting the death rate.

3.9.7 References

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3.10 ZOOPLANKTON

Attempts to understand algal population dynamics and nutrient cycling in surface waters generally require a parallel and simultaneous understanding of herbivorous zooplankton population dynamics. The term "zooplankton," however, encompasses a large variety of forms of animal plankton, not all of which are herbivorous. Some have the ability to photosynthesize. Some are predatory, while some are not. Some forms are seasonal with a dormant period, and some overwinter by forming cysts. Some are microscopic, and some are easily visible to the naked eye. The zooplankton species composition in any water body is highly mutable, being dependent to a large extent upon such factors as phytoplankton population dynamics, availability of organic particulate matter, bacterial populations, temperature, and salinity. Prior to discussing population dynamics, models, and constants, it is important to understand the extreme complexity of zooplankton-biotic community relationships. Such an understanding should lead to an appreciation for the degree of simplification necessary in developing a practical model as well as an understanding of what such a model can and cannot do.

3.10.1 Important Zooplankton Organisms

Freshwater zooplankton populations are generally dominated by the cladocera and copepoda (two crustaceans) and by the rotifers, with a number of other forms being important under some circumstances. The latter include the protozoans and some forms having only part of their life cycles as zooplankton. Organisms which are zooplanktonic only as part of their life cycles include some kinds of flatworms, aquatic insects, mites, gastrotrichs, and coelenterates. Some fish also spend part of their life cycles as organisms which can truly be termed zooplankton.

According to Wetzel (1975), the protozoans can sometimes represent a significant proportion of the total numbers and biomass of zooplankton. Wetzel cites data from Lake Dalnee, a large lake in Kamchatka, Siberia (U.S.S.R.), where the midsummer pelagial zooplankton population had a large flagellate and ciliate protozoan component. Their maximal biomass was observed to coincide with a decline in a summer algal bloom and with a bloom of bacterial forms. The protozoans were also observed to occur in distinct layers in the water column.

According to Wetzel, the Lobosan Rhizopod Difflugia occurs commonly in both oligotrophic and eutrophic lakes. A number of ciliate protozoans may represent important components of zooplankton numbers, but usually only in shallow lakes or in anaerobic hypolimnia. The rotifers, in contrast, are generally an important component of freshwater zooplankton populations, are commonly sessile (attached) and tend to be associated with littoral substrates (Wetzel, 1975). Numbers tend to be quite high where associated with small submersed macrophytes, as opposed to situations where the organisms are more exposed and subject to predation. The sessile organisms undergo a number of morphological changes in going from the sessile to planktonic form. For example, there is commonly a weight reduction with simultaneous volume increase. Swimming apparatus are developed along with other swimming adaptations such as those which reduce the sinking rate. Among rotifers which are sessile during part of their life cycles and those which are entirely planktonic, the free-swimming forms commonly are ciliated, the cilia providing for locomotion as well as feeding functions.

The seasonal behavior of rotifer populations is complex. Some forms are perennial while others (the stenotherms) bloom in winter and early spring. Still others bloom in summer in response to food availability. Wetzel cites data for Vorderer Finstertaler See, a deep alpine drainage lake in Austria, which has two rotifers constituting 99 percent of the zooplankton population. One of the two rotifers (Keratella humalis) is a stenotherm, blooming in midwinter and declining in warmer weather. The other rotifer (Polyarthra dolichoptera) is also a coldwater form which tolerates anoxic conditions. It was found to dominate in midsummer.

According to Wetzel, the seasonal distribution of rotifer populations is likely to vary considerably from lake to lake in a given geographical area, and the populations are likely to be only very generally synchronous among such lakes.

In fresh water, the crustacean zooplankters are dominated by the Cladocerans and Copepoda. The freshwater Branchiopoda (fairy and clam shrimps) are common planktonic forms in shallow saline inland waters, particularly playas in semiarid regions.

The Cladocerans are generally very small (microzooplankton) having a highly variable seasonality. Some are perennial, while some survive cold periods through a resting egg stage. Some Cladocerans are coldwater forms living in northerly lakes and commonly tolerating low dissolved oxygen concentrations.

Wetzel cites population dynamics data for Base Line Lake, Michigan, as a typical case. The zooplankton population consisted mainly of Daphnia. Two population maxima were observed in Daphnia galeata mendotae. The first occurred in the spring, and the second occurred late in autumn. This species overwintered in the free-swimming form rather than as a resting stage. The birth rates in spring and autumn were nearly equal. In winter, reproduction ceased and a slow death rate determined populations over time. During the summer, predation by the large Cladoceran Leptodora was found to be important.

In late summer, Daphnia retrocurva bloomed, greatly exceeding D. galeata. D. retrocurva and D. catawba were found to have late summer maxima. Both overwinter in the egg stage. The presence of D. catawba in late summer and resulting competition with D. galeata was deemed responsible for delaying the autumnal maximum of the latter.

In a shallow, eutrophic lake in northwestern Pennsylvania (Sanctuary Lake), D. galeata exhibited maxima similar to those observed in Michigan. Again D. retrocurva was codominant in late summer, and the predaceous Leptodora kindtii grazed the Daphnia down in summer. The population dynamics of Leptodora were correlated with loss rates of prey. The predators were found to shift seasonally among Daphnia, Ceriodaphnia, Bosmina, and Chydorus and the copepods Cyclops and Diaptomus (Wetzel, 1975).

Like the rotifers, the Cladocera exhibit seasonal polymorphism. Although cyclomorphic growth patterns in these organisms do not mean the difference between sessile and planktonic habit, they do, as was true with rotifers, influence vulnerability to predation. In rotifers, the free-swimming form is likely to be more vulnerable than the sessile form. In Daphnia, changes appear to make the organism less conspicuous, and therefore less likely to be consumed by fish.

The Harpacticoid copepods are almost entirely associated with macroscopic vegetation and particulate organic matter in the littoral zone. The planktonic Cyclopoid copepods form major components of the copepod zooplankton, particularly in small shallow lakes. The Cyclopoid copepods are primarily littoral benthic species. The Calanoid copepods, on the other hand, are almost exclusively pelagial zone plankton.

Some Cyclopoid copepods are known to have diapause periods at either the egg or copepodite stage, with or without encystment (Wetzel, 1975). In some, the diapause occurs in winter while in some, it is in summer. In Cyclops strenuus strenuus, the reproduction characteristics result in a bimodal population over the year. Cyclops strenuus abyssorum, on the other hand, has only a single reproductive period per year.

Coexisting Cyclopoid copepod species exhibit asynchronous maxima and diapause periods, which is believed to minimize competition. The coexistence mechanisms include seasonal separation, vertical separation, and differences in terms of food particle sizes taken.

3.10.2 Modeling Zooplankton

A popular method for representing zooplankton assemblages is through use of Michaelis-Menton formulations analogous to those used in modeling phytoplankton. The zooplankton are assumed to grow in accord with food availability. The food, in turn, is presumed to be algae, despite the very much more complex trophic relationships which usually exist in the prototype (see Section 3.10.2.1.1).

The zooplankton, in turn, are preyed upon by higher levels in the food chain, and undergo endogenous respiration and death. It is clear, based upon known predator-prey relationships that the monotonic food chain is artificial, and represents a gross oversimplification of reality. The defense of the models, however, lies in practicality and the fact that for most purposes, simplified models lead to satisfactory estimates.

Zooplankton biomass concentrations are generally assumed to be influenced by the following processes: a) growth, b) respiration, c) grazing by higher trophic levels, and d) death. As with typical phytoplankton representations, these processes are usually combined in a source/sink formulation which is then included in a complete mass balance expression.

The source/sink formulation accounting for changes in zooplankton concentration is of the following general form in the majority of water quality models:

$$\frac{dZ}{dt} = \left(G_z - D_z\right) Z \tag{3-127}$$

where G_z = gross specific growth rate, day^{-1}

D_z = death rate, day^{-1}

Z = zooplankton concentration, mg/l

3.10.2.1 Gross Specific Growth Rate

There are a variety of formulations commonly used to compute the gross specific growth rate. The formulations incorporate varying degrees of complexity, and the variation is often the major reason for differences among formulations reported by various researchers.

Generally, the rate, G_Z, is considered to be a function of algal density, ingestion or grazing rate, and assimilation efficiency. Food material is typically assumed to flow through a zooplankton system according to the following schematic (Lombardo, 1972):

FOOD → GRAZING → INGESTION → ASSIMILATION (GROWTH)
(FILTERING) → EXCRETION

where INGESTION = GRAZING (FILTERING) RATE X FOOD CONCENTRATION

ASSIMILATION = ASSIMILATION EFFICIENCY X INGESTION

3.10.2.1.1 Factors Affecting G_Z

Feeding mechanisms and food availability are a primary determinant of growth rates. Some models which incorporate phytoplankton and zooplankton assume a single filtering rate of the phytoplankton by the zooplankton. Others account for more than one feeding mechanism. Regardless of the assumed model, the mechanism of grazing is an important consideration in computing G_Z, as is the type of food preferentially sought.

Most protozoan forms of zooplankton feed on bacteria, algae, particulate detritus and other protozoans. Some are carnivorous, feeding on small metazoans (Wetzel, 1975). Mechanisms of ingestion are generally through pinocytosis and formation of food vacuoles. Some protozoans are known to feed actively on algae. Amoeboid forms are also known to consume diatoms.

Rotifers feed by sedimenting seston particles into the mouth orifice by means of the pulsating action of the coronal cilia. There is a considerable variation in the size of food particles consumed, with most particles being less than about 12 microns in diameter. Larger cells, some being up to 50 microns in diameter, however, are sometimes ruptured to release cell particulate matter (Wetzel, 1975). Asplanchna is a raptorial rotifer which seizes and ingests whole cells or at least cell contents of algae, other rotifers, and small planktonic crustaceans. According to Wetzel (1975), some algae, such as Chlorella, are not eaten as readily as others, possibly due to some negative physiological response elicited by the algal cell content.

Feeding among the crustacean zooplankters is usually through filtering of particles by the setae. The food collects in the ventral food groove, and is moved forward to the mouth.

Some forms, particularly species of Polyphemus and Leptodora, are predaceous and feed on protozoa, rotifers, and small crustaceans. Recent research has suggested that some zooplankton forms have the ability to select food for consumption and that such selection can well affect which phytoplankton will bloom and which will not (Wetzel, 1975).

The mouth parts of the Harpacticoids are adapted for seizing large particles and scraping food from them. No filtering mechanism occurs in free-living Cyclopoida. Feeding is raptorial. The carnivorous Cyclopoida include the Macrocyclops, Acanthocyclops, Cyclops, and Mesocyclops. Herbivorous Cyclopoida include Microcyclops, Acanthocyclops, and Eucyclops, which feed upon a variety of algae (Wetzel, 1975).

The quantity of food consumed by zooplankton is not quantitatively converted to biomass. Most models account for this through an assimilation factor. However, assimilation efficiencies vary as a function of ambient conditions. The assimilation efficiency has been found, for example, to decrease with increasing food concentration. The assimilation efficiency has also been found to decrease with decreasing caloric food value, representative of detritus and non-nutritious particles in the water. Lombardo (1972) reported that healthy algae have a caloric value of about 5 calories/mg dry weight.

At high phytoplankton concentrations, the zooplankton do not metabolize all the phytoplankton grazed, but rather, they excrete a portion in undigested form. According to Wetzel (1975), ingestion of algae does not always mean that the cells will be assimilated. Algae that have especially resistant cell walls, gelatinous sheaths, or masses of colonial cells can pass through the gastric tract of some zooplankton in viable form. In some cases, individual cells may be assimilated while colonies of the same algal species pass through relatively unaltered.

Another factor affecting G_Z is water temperature. As was true for phytoplankton, rates of growth of zooplankton are influenced by biochemical reaction rates. These rates determine the speed of swimming, the rate of feeding and filtering, the rate of assimilation, and the rate of excretion.

3.10.2.1.2 Formulations for Computing G_z

Many investigators (see, for example, Tetra Tech, 1975, U.S. Army Corps of Engineers, 1974, Bierman, 1976, O'Connor, et al., 1975, and Orlob, 1974) have used Michaelis-Menton terms in their growth formulations. This type of representation may be illustrated by considering the following general form of the Michaelis-Menton expression as given by Thomann, et al., (1975):

$$G_z = A_{zp} \, C_g \, K_{mp} \left(\frac{P}{K_{mp} + P} \right) \qquad (3\text{-}128)$$

where A_{zp} = assimilation efficiency relating phytoplankton biomass ingested to zooplankton biomass produced, unitless

C_g = filtering rate @ 20°C, ℓ/mg-chl-day

K_{mp} = phytoplankton biomass concentration at which the growth rate, G_Z, is half the maximum possible growth rate, mg-chl/ℓ

P = phytoplankton biomass concentration, mg-chl/ℓ

The filtering rate of zooplankton which use a filtering mechanism varies according to a number of factors. These include:

- food particle size
- food particle density
- acceptability of food
- temperature
- species of zooplankton

In addition, some zooplankton are known to filter intermittently, and, possibly, only during darkness (Lombardo, 1972). Lombardo also reported that when filter feeding crustaceans encounter low food concentrations, the feeding rate is limited by the ability of the animal to filter water.

The phenomenon of variable assimilation efficiency is accommodated with the following functional relationship:

$$A_{zp}\left(\frac{K_{mp}}{K_{mp} + P}\right) \tag{3-129}$$

By multiplying this term by the biomass term, C_gP, the specific growth rate expression given in Equation (3-128) is obtained.

Under conditions of nonlimiting food sources, i.e., when $P >> K_{mp}$, the growth expression (Equation (3-128)) reduces to:

$$A_{zp}\ C_g\ K_{mp}$$

which is the "zooplankton maximum growth rate" for saturating phytoplankton concentrations.

In Equation (3-128), phytoplankton biomass is measured as mg-chl/ℓ while zooplankton biomass is measured as mg-C/l. Therefore a carbon to chlorophyll ratio (A_{zp}) must be specified. In model applications to five different locations (San Joaquin River, San Joaquin Delta and Potomac Estuaries, and Lakes Erie and Ontario), a value of 50 was used.

Baca and Arnett (1976) use the following expression for zooplankton specific growth rate based on the formulations given by Thomann, O'Connor, and Di Toro:

$$G_z = A_{zp}\ C_g\left(P/\left(K_{mp} + P\right)\right) \tag{3-130}$$

where C_g = zooplankton grazing rate, day^{-1}

The specific growth rate expression proposed by Bierman (1976) has a similar form:

$$G_z = \text{RZMAX} \cdot A_{zp} \cdot \sum_{L=1}\left\{\frac{\text{ZEFF (K,L)} \cdot \text{A(L)}}{\text{KZSAT (K,L)} + \sum\limits_{L=1}^{n} \text{ZEFF (K,L)} * \text{A(L)}}\right\} \tag{3-131}$$

where n = number of phytoplankton species

RZMAX = zooplankton maximum ingestion rate, day^{-1}

A_{zp} = zooplankton assimilation efficiency, unitless

ZEFF(K,L) = ingestion efficiency of zooplankton species K for phytoplankton species L, unitless

KZSAT(K,L) = half-saturation concentration of phytoplankton L for grazing by zooplankton K, mg/l

A(L) = phytoplankton L concentration, mg/l

Bierman's model considers two separate groups of zooplankton which can graze upon two distinct groups of phytoplankton. The two zooplankton types are differentiated on the basis of maximum ingestion rates. The formulation for gross specific growth rate is actually a form of the expression used by Baca and Arnett (1976) (Equation (3-130)) with two modifications. First, the term ZEFF(K,L) in the Bierman formulation is used to accommodate zooplankton preference for one type of phytoplankton over another. Second, the summation of a number of Michaelis-Menton terms is incorporated to allow consideration of the limiting influence on total growth of the availability of specific phytoplanktonic groups.

Tetra Tech (1975, 1976), Chen and Wells (1975), and the U.S. Army Corps of Engineers (1974) use the following formulation for the zooplankton specific growth rate:

$$G_z = ZMAX\left(ALG/(ALG_2 + ALG)\right) \tag{3-132}$$

where ZMAX = maximum specific growth rate @ 20°C, day^{-1}

ALG_2 = half-saturation constant for zooplankton grazing on algae, mg/l

ALG = effective algal concentration, mg/l

$= ALG1 + ALG2\left(\frac{PREF\ 2}{PREF\ 1}\right)$

ALG1 = concentration of type 1 algae, mg/l

ALG2 = concentration of type 2 algae, mg/l

PREF 1 = preference for zooplankton grazing on type 1 algae, decimal

PREF 2 = preference for zooplankton grazing on type 2 algae, decimal

Equation (3-132) can be made analogous to Equation (3-128) if ZMAX is set equal to the quantity $A_{zp} C_g K_{mp}$. As previously illustrated, the quantity $A_{zp} C_g K_{mp}$ from Thomann, O'Connor and Di Toro's expression represents a maximum growth rate under saturated phytoplankton conditions.

Tetra Tech (1975, 1976), Bierman (1976), and the U.S. Army Corps of Engineers (1974) have included phytoplankton species preferences in their formulations. This addition was necessary because more than one species of phytoplankton were considered. In Tetra Tech's model, the zooplankton feeding preference is used to establish a single effective algal concentration. This simplification allows input of only one half-saturation constant for zooplankton growth and adjustment of the concentration of algae accordingly.

Canale, *et al*. (1976) propose a complex zooplankton model which considers the following nine different types of zooplankton:

1. *Leptodora* and *Polyphemus* (predators)		RAPTORS
2. *Cyclops* (small omnivores)		
3. *Cyclops*	nauplii	SELECTIVE FILTERERS
4. *Diaptomus*		
5. *Limnocalanus* and *Epischura*		
6. *Diaptomus* (small herbivorous copepods)		
7. *Limnocalanus* and *Epischura* (large omnivores)		
8. *Daphnia* (large herbivorous cladocerans)		NON-SELECTIVE FILTERERS
9. *Bosmina* and *Holopedium* (small herbivorous cladocerans)		

Conceptually, the model is similar to those previously described. The specific growth rate formulation, in qualitative terms, can be described as the product of an ingestion rate, or "eating rate" as it is called by Canale, and an assimilation efficiency. In equation form, it becomes:

$$G_z = C_z \cdot \begin{pmatrix} \text{assimilation} \\ \text{efficiency} \end{pmatrix}_z \begin{pmatrix} \text{eating} \\ \text{rate} \end{pmatrix}_z \qquad (3\text{-}133)$$

where C_z = zooplankton concentration for zooplankton type z, mg/l

The assimilation efficiency represents milligrams zooplankton carbon developed per milligram of food carbon consumed and the eating rate represents milligrams of food carbon consumed per milligram of zooplankton carbon per day.

Much of the complexity of the formulation is due to the inclusion of three different types of eating (grazing) behavior - raptorial, selective filtering, and non-selective filtering. For raptors, the eating rate expression is given as:

$$\begin{pmatrix}\text{eating}\\ \text{rate}\end{pmatrix}_z = A7_z \, \phi_z(T) \left(\frac{\sum_i C_i}{\sum_i C_i + KFOOD_z} \right) \qquad (3\text{-}134)$$

where $\sum_i C_i$ = sum of concentrations of all states (i) that can serve as food for raptor state z

$KFOOD_z$ = food level half-saturation constant for state z (raptors), mg food C/l; typically 0.2

$A7_z$ = snatching rate at 20°C, mg food C/mg zoopl. C-day (0.70 - *Leptodora* and *Polyphemus*, 0.43 - *Cyclops*)

$\phi_z(T)$ = temperature correction term, unitless

The eating expression for selective filterers is:

$$\begin{pmatrix}\text{eating}\\ \text{rate}\end{pmatrix}_z = A7_z \, \phi_z(T) \left(\frac{A9 \cdot \sum_i C_i + A10}{\sum_i C_i + A10} \right) \sum_i C_i \qquad (3\text{-}135)$$

where A9 = minimum filtering rate multiplier, unitless; typically 0.1

A10 = food level where multiplier is 1/2 (1+A9) $\frac{\text{mg food C}}{\text{l}}$; typically 0.2

$A7_z$ = maximum filtering rate, l/mg zoopl. C-day:

2.6 - *Cyclops nauplii*
6.5 - *Diaptomus nauplii*
5.2 - *Limnocalanus* and *Epischura nauplii*
1.0 - *Diaptomus*
1.25 - *Limnocalanus* and *Epischura*

And for non-selective filterers, the expression is:

$$\begin{pmatrix}\text{eating}\\ \text{rate}\end{pmatrix}_z = A7_z\ \phi_z(T)\ \sum_i C_i \qquad (3\text{-}136)$$

Nonselective filterers cannot lower their filtering rate when the plankton content of the water increases. Therefore, they operate below the maximum possible efficiency. The assimilation efficiency for non-selective filterers is given by the following expression:

$$\begin{pmatrix}\text{assimilation}\\ \text{efficiency}\end{pmatrix}_z = A11N\left(\frac{A24}{\sum\limits_i C_i + A24}\right) \qquad (3\text{-}137)$$

where A11N = maximum efficiency possible, mg zoopl. C/mg food C; typically 0.8

A24 = half-maximum efficiency food level for nonselectives, mg food C/l; typically 0.2

Species preference is accommodated by means of the following expression:

$$\begin{pmatrix}\text{preference of species } z\\ \text{for species } k\end{pmatrix} = \frac{\alpha_k^z\ C_k}{\sum\limits_i \left(\alpha_i^z\ C_i\right)} \qquad (3\text{-}138)$$

The electivity, α_k^z, is defined as the fraction of species z diet that would be composed of food species k if all food species were present in equal concentrations. The preference of z for k is proportional to the product of the electivity of species z for species k and the concentration of species k(i.e., C_k). Electivities used in Canale's model are unverified.

3.10.2.1.3 Growth Rate Data

Table 3-44 provides values for the zooplankton maximum specific growth rate, conversion efficiency, grazing rate, Michaelis-Menton half-saturation constant, and chemical composition. Tables 3-45 through 3-48 show filtering rates for various zooplankton forms. Tables 3-49 and 3-50 give production data for both herbivorous and predatory zooplankton. Table 3-51 gives food utilization efficiencies for several zooplankton forms.

TABLE 3-44. VALUES FOR COEFFICIENTS IN MICHAELIS-MENTON ZOOPLANKTON GROWTH FORMULATIONS

Zooplankton Description	Zooplankton Maximum Specific Growth Rate (day^{-1})	Zooplankton Conversion Efficiency, A_{zp} (decimal)	Zooplankton Grazing Rate	Michaelis-Menton Half-Saturation Constant	Chemical Composition (fraction by weight) C	N	P	Location of Study	Reference
Zooplankton	-	0.5-0.7	0.05-0.2 day^{-1}	0.06-0.6 mg-C/l		-		-	Baca and Arnett (1976)
Zooplankton	0.30	-	-	0.4 mg/l	0.4	0.08	0.015	North Fork Kings River, California	Tetra Tech, Inc. (1976)
Zooplankton	0.15-0.30	-	-	0.4-0.6 mg/l		-		-	U.S. Army Corps of Engineers (1974)
Zooplankton	0.15	-	-	0.5 mg/l		-		Lake Washington	Chen and Orlob (1975)
Zooplankton	-	0.6	0.35-0.50 day^{-1}	-		-		-	Bierman (1976)
Raptor Feeders	-	0.4	-	-		-		-	Canale et al. (1976)
Selective Filtering Feeders	-	0.7	-	-		-		-	Canale et al. (1976)
Zooplankton	-	0.6	0.13 l/mg-C-day	50 μg chlor/l		-		San Joaquin River, California	O'Connor et al. (1975)
Zooplankton	-	0.6	0.18 l/mg-C-day	50 μg chlor/l		-		San Joaquin Delta Estuary, California	O'Connor et al. (1975)
Zooplankton	-	-	-	-		-		Potomac Estuary	O'Connor et al. (1975)
Zooplankton	-	0.65	0.25 l/mg-C-day	50 μg chlor/l		-		Lake Erie	O'Connor et al. (1975)
Zooplankton	-	0.60	1.2 l/mg-C-day	10 μg chlor/l		-		Lake Ontario	O'Connor et al. (1975)
Zooplankton	0.25	-	-	0.5 mg/l		-		San Francisco Bay Estuary	Chen (1970)
Zooplankton	0.25	-	-	0.5 mg/l	0.5	0.09	0.015	Boise River, Idaho	Chen and Wells (1975)
Zooplankton	-	0.6	0.5 l/mg-dry wt-day	0.06 μg chlor/l		-		-	Di Toro et al. (1971)

TABLE 3-45. VALUES FOR ZOOPLANKTON FILTERING RATES (AFTER LOMBARDO, 1972)

Feeding Organism	Food Organism	Temperature (°C) Filtering Rate (ml/mg dry wt-hr				
Acartia tonsa	*Thalassiosira fluviatius*	2°	8°	15°	22.5°	
	800-100 cell/ml and *Artemia*	17.0	33.0	58.0	92.0	
Centropages hamatus	*Thalassiosira fluviatius* 800-100 cell/ml and *Artemia*	8.3	9.0	10.0	35.0	
C. typicus	*Thalassiosira Fluviatius* 800-100 cell/ml and *Artemia*	6.7	13.2	11.2	20.0	
Daphnia magna	*Rhodotorula glutinis*	15°	20°	25°		
	.25 x 10^5 cells/ml	8.0	16.6	19.0		
D. schodleri	*Rhodotorula glutinis* .25 x 10^5 cells/ml	12.6	15.9	11.3		
D. pulex	*Rhodotorula glutinis* .25 x 10^5 cells/ml	13.6	15.9	12.8		
D. galeata	*Rhodotorula glutinis* .25 x 10^5 cells/ml	10.3	24.3	27.9		
D. rosea[1]	*Rhodotorula glutinis*	5°	10°	15°	20°	25°
	.25 x 10^5	13.8	18.0	25.0	28.4	26.2
D. rosea	Mixture of *Scenedesmus*,	5°	12°	14°	20°	25°
	other algae and bacteria	18.4	26.0	27.0	22.2	21.0

[1] 0.040 mg/animal was used.

TABLE 3-46. COMPARISON OF FILTERING RATES OF VARIOUS CLADOCERAN ZOOPLANKTERS (AFTER WETZEL, 1975)

Species	Type of Food	Animal Size Range (Length in mm)	Average Filtering Rate (ml animal^{-1} day^{-1})	Source
Daphnia				
D. rosea	In situ phytoplankton	1.3-1.6	5.5	Haney (1973)
			3.6	Burns and Rigler (1967)
D. galeata		1.5-1.7	6.4	Haney (1973)
			3.7	Burns and Rigler (1967)
D. parvula		0.7-1.2		
D. longispina			3.8	Haney (1973)
			2.3	Nauwerck (1963)
Ceriodaphnia				
C. quadrangula		0.7-0.9	4.6	Haney (1973)
Diaphanosoma				
D. brachyurum		0.9-1.4	1.6	Haney (1973)
Bosmina				
B. longirostris		0.4-0.6	0.44	Haney (1973)
Chydorus				
C. sphaericus		0.1-0.2	0.18	Haney (1973)

TABLE 3-47. FILTERING RATES AND CONTRIBUTION TO TOTAL GRAZING OF SPECIES. DOMINANT ZOOPLANKTON OF ACIDIC DROWNED BOG LAKE, ONTARIO, IN EARLY SEPTEMBER[a] (AFTER WETZEL, 1975)

Species	Filtering Rates (ml animal^{-1} day^{-1})		Species Contribution to Total Grazing (%)	
	Sept.1968	Sept.1969	Sept.1968	Sept.1969
Bosmina longirostris	0.46	0.45	85	44.8
Holopedium gibberum	-	9.4	12	46.2
Daphnia parvula	-	1.6	0.1	7.5
Diaptomus oregonensis	-	2.1	2.0	0.9
Diaphanosoma brachyurum	-	1.2	0.1	0.4

[a] Data extracted from Haney (1973).

TABLE 3-48. COMPARISON OF FILTERING RATES OF VARIOUS COPEPODS (AFTER WETZEL, 1975)

Species	Type of Food	Particle Concentration (cells x 10^{-3} ml^{-1})	Filtering Rate (ml $animal^{-1}$ day^{-1})	Source
Diaptomus				
D. graciloides	Natural phytoplankton	-	0.3-2.8	Nauwerck (1959)
	Scenedesmus	13.6	4.1	Malovitskaia and Sorokin (1961)
D. siciloides	*Pandorina* and *Chlamydomonas*	-	2.0	Comita (1964)
D. oregonensis	*Chlamydomonas*	1.5-25.0	2.5	Richman (1966)
		25.0-52.0	2.5-1.4	
	Chlorella	52.0-198.0	1.4-0.3	
	In situ phytoplankton	-	1.4-0.00	Haney (1973)
D. gracilis	*Melosira* and *Asterionella*	24.2-52.0 198.0	1.92-1.96 0.68	Malovitskaia and Sorokin (1961)
	Chlorella	<30.0	0.61 (5°C) 1.51 (12°C) 2.40 (20°C)	Kibby (1971)
	Scenedesmus	<30.0	0.94 (12°C) 1.32 (20°C)	
	Diplosphaeria	<30.0	1.76 (12°C) 2.54 (20°C)	
	Ankistrodesmus	<30.0	1.61 (12°C) 2.45 (20°C)	
	Carteria	<30.0	0.87 (20°C)	
	Nitzschia	<30.0	1.96 (20°C)	
	Pediastrum	<30.0	0.02 (20°C)	
	Haematococcus	<30.0	2.16 (20°C)	
	Bacteria	<30.0	0.19 (20°C)	
Limnocalanus				
L. macrurus	*Scenedesmus*	-	2.45 (<5°C)	Kibby and Rigler (1973)
	Chlamydomonas	-	1.24 (<5°C)	
	Rhodoturula (yeast)	-	0.1 (<5°C)	

TABLE 3-49. EXAMPLES OF THE PRODUCTION OF HERBIVOROUS AND PREDATORY ZOOPLANKTON COMMUNITIES (AFTER WETZEL, 1975)

Lake Type	Period of Investigation	Biomass (B)[a] g m^{-3}	Biomass (B)[a] kcal m^{-3}	Production (P)[a] g m^{-3}	Production (P)[a] kcal m^{-3}	Biomass Turnover Time (days) Average	Biomass Turnover Time (days) Range	Remarks and Source
OLIGOTROPHIC								
Lake Baikal, USSR	June-July	0.136						Primarily *Epischura*; Moskalenko and Votinsev (1970)
	Sept.	0.43						
	Annual (0-50 m depth)	-		3.44	-			
Clear Lake, Ontario	Annual	0.20		3.02	16.435	25	12-333	Herbviorous zooplankton (rotifers, *Holopedium*, *Daphnia*, *Bosmina*, *Diaptomus*); Schindler (1970)
Lake 239, Ontario	May-Nov.	-		0.61	3.331	22	10-91	
Lake Krugloe, USSR	Annual		0.405	0.94	5.116	29		Arctic lake; Winberg (1970)
MESOTROPHIC								
Taltowisko Lake, Poland	May-Oct.	0.12		3.04		14.3		29 of total lake area in littoral zone; Kajak, *et. al.* (1970); Kajak (1970)
Herbivores				4.68	25.43	10.2		
Predators				0.46	2.50	9.1		
Lake Naroch, USSR	**Annual**	0.07	0.38	1.12	6.11	22.4		**Winberg (1970)**
Lake Krasnoe, USSR	**Annual**	0.14	0.76	3.09	16.82	16.5		
EUTROPHIC								
Lake Mikolajskie, Poland	May-Oct.							Kajak, *et al.* (1970); Hillbricht-Ilkowska, *et al.* (1970)
Herbivores				6.45	35.09	9.2	4.0-12.5	
Predators				1.32	7.18	25.0		
Lake Sniardwy, Poland	May-Oct.							
Herbivores				3.08	16.78	14.9	8.3-33	
Predators				0.50	2.71	14.3		
Kiev Reservoir, USSR								
Herbivores		0.35	1.9	9.15	49.8	13.9		Winberg (1970)
Predators		0.072	0.12	1.16	6.3			
Severson Lake, Minnesota	May-Oct.							Comita (1972)
Herbivores				2.51	13.66			
Predators				0.11	0.60			
DYSTROPHIC (high dissolved organic matter)[b]								
Lake Flosek, Poland	May-Oct.							*Sphagnum* bog; high littoral and allochthonous organic inputs; Kajak, *et al.* (1970); Hillbricht-Ilkowska, *et al.* (1970)
Herbivores				25.68	139.7	6.3		
Predators				1.16	6.3	25.0		

[a] Estimated using the mean caloric value for microconsumers (Cummins and Wuycheck, 1971).

[b] See discussion in Chapter 18 of Wetzel (1975).

TABLE 3-50. EXAMPLES OF PRODUCTIVITY OF HERBIVOROUS AND PREDATORY FORMS OF ZOOPLANKTON (AFTER WETZEL, 1975)

Type/Species	Lake; General Productivity	Period of Investigation	Production Estimates^a g m^{-3} day^{-1}	Production Estimates^a kcal m^{-2} day^{-1}	Biomass Turnover Time (Days) Average	Biomass Turnover Time (Days) Range	Source
FILTER FEEDERS:							
Cladocera:							
Daphnia hyalina	Eglwys Nynydd Reservoir, Wales; eutrophic	Annual, 1970	0.57		21.3	3.8-333	George and Edwards (1974)
		Annual, 1971	0.32		15.9		
D. parvula	Severson Lake, Minn.; eutrophic	Annual	0.010	0.102	-		Comita (1972)
D. galeata mendota	Sanctuary Lake, Pa.; eutrophic reservoir	May-Nov., 1966	0.407	3.026			Cummins, et al. (1969)
		May-Nov., 1967	0.030	0.223			
	Canyon Ferry Reservoir, Mont.; eutrophic	April-Sept.	0.114		10.0		Wright (1965)
D. schodleri	Canyon Ferry Reservoir, Mont.; eutrophic	April-Sept.	0.227		6.7		Wright (1965)
D. longispina	Lake Sevan, southern USSR	Annual	0.006		58.9		Meshkova (1952) in Winberg (1971)
Bosmina longirostris	Severson Lake, Minn.	Annual	0.007	0.071	-		Comita (1972)
B. longirostris and *B. coregoni*	Sanctuary Lake, Pa.	May-Nov., 1966	0.183	1.361			Cummins, *et al*. (1969)
		May-Nov., 1967	0.067	0.498			
Ceriodaphnia reticulata		July-Nov.	0.031	0.154			
Chydorus sphaericus		July-Aug., 1966	0.004	0.020			
		July-Aug., 1967	0.047	0.233			
Cladocera	Naroch Lake, USSR	May-Oct.	0.0026	0.117	13.7		Winberg, *et al*. (1970)
	Myastro Lake, USSR	May-Oct.	0.015	0.403	10.9		
	Batorin Lake, USSR	May-Oct.	0.033	0.484	10.5		
Copepods:							
Cyclops strenuus	Buttermere, England; oligotrophic	Annual	0.0004				Smyly (1973)
	Rydal Water, England; eutrophic	Annual	0.0005				
	Grasmere, England; eutrophic	Annual	0.0006				
	Esthwaite Water, England; eutrophic	Annual	0.0017				
	Lake Sevan, southern USSR	Annual	0.0007		79.3		Meshkova (1952) in Winberg (1971)
Eudiaptomus graciloides	Naroch Lake, USSR	May-Oct.	0.0010	0.044	24.7		Winberg, *et al*. (1970)
	Myastro Lake, USSR	May-Oct.	0.0065	0.174	20.2		
	Batorin Lake, USSR	May-Oct.	0.0070	0.104	15.4		
Mesocyclops edax	Severson Lake, Minn.	Annual	0.0046	0.045	-		Comita (1972)
Diaphanosoma leuchtenbergianum			0.0067	0.067	-		
Diaptomus siciloids			0.0342	0.341	-		
Arcthodiaptomus (2 species)	Lake Sevan, southern USSR	Annual	0.0014	-	162		Meshkova (1952) in Winberg (1971)

(continued)

TABLE 3-50 (continued)

Type/Species	Lake; General Productivity	Period of Investigation	Production Estimates[a]		Biomass Turnover Time (Days)		Source
			$g\ m^{-3}\ day^{-1}$	$kcal\ m^{-2}\ day^{-1}$	Average	Range	
FILTER FEEDERS: (Cont.)							
Rotifers:							
Keratella quadrata	Severson Lake, Minn.	Annual	0.0021	0.021	-		Comita (1972)
K. cochlearis			0.0007	0.0074	-		
Filinia longiseta			0.0011	0.0112	-		
Brachionus sp.			0.0075	0.0752	-		
Polyarthra sp.			0.0010	0.0103	-		
Rotifers	Naroch Lake, USSR	May-Oct.	0.0027	0.120	1.7		Winberg, et al. (1970)
	Myastro Lake, USSR	May-Oct.	0.0024	0.065	3.9		
	Batorin Lake, USSR	May-Oct.	0.0105	0.156	2.6		
PREDATORY FEEDERS:							
Cladocera:							
Leptodora kindtii	Sanctuary Lake, Pa.	May-Nov., 1966	0.003	0.022	-		Cummins, et al. (1969)
		May-Nov., 1967	0.013	0.097	-		
Cladocera	Naroch Lake, USSR	May-Oct.	0.0003	0.013	11.3		Winberg, et al. (1973)
	Myastro Lake, USSR		0.0009	0.023	3.9		
	Batorin Lake, USSR		0.0002	0.003	10.8		
Copepods:							
Cyclops sp.	Naroch Lake, USSR	May-Oct.	0.0008	0.034	9.7		
	Myastro Lake, USSR		0.0023	0.062	19.4		
	Batorin Lake, USSR		0.0094	0.140	14.2		
Rotifers:							
Asplanchna priodonta	Naroch Lake, USSR	May-Oct.	0.0014	0.061	2.9		
	Myastro Lake, USSR		0.0061	0.163	2.5		
	Batorin Lake, USSR		0.0105	0.156	3.2		
Asplanchna sp.	Severson Lake, Minn.	Annual	0.0031	0.031	-		Comita (1972)
Synchaeta sp.			0.00009	0.0009	-		
Insect larvae:							
Chaborus punctipennis			0.0001	0.001	-		

[a] Conversions estimated using the caloric mean of microconsumers (Cummins and Wuycheck (1971)), when mean depths available.

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TABLE 3-51. EXEMPLARY ESTIMATES OF EFFICIENCIES OF FOOD UTILIZATION BY VARIOUS ANIMALS[a] (AFTER WETZEL, 1975)

		% of Ingested Food Utilized in:			% of Assimilated Energy Expended in:		
Organisms	Egestion	Assimilation	Respiration	Growth and Reproduction	Respiration	Growth and Reproduction	Source
ZOOPLANKTON							
Daphnia pulex	69-86	14-31	4-14	10-17	27-44	56-73	Richman (1958)
Ceriodaphnia reticulata	-	10.6	1.8	-	-	-	Czeczuga and Bobiatynska-Ksok (1970)
Simocephalus vetulus							Klekowski (1970)
Juveniles (♀)	27.6	72.4	19.5	52.9	26.9	73.1	
Reproducing (♀)	68.3	31.7	11.2	20.5	35.3	64.7	
Leptodora kindtii	60.0	40.0	-	-	92.7	7.3	Cummins, *et al.* (1969); Moshiri, *et al.* (1969)
Mesocyclops albidus	-	20-75	ca 20	ca 25	ca 50	ca 50	Klekowski and Shushkina (1966)
10 Herbivores	52.4	47.6	40.1	7.5	-	-	Comita (1972)
BENTHIC ANIMALS							
Asellus aquaticus	69.7	30.3	24.7	5.6	81.8	18.2	Klekowski (1970)
Lestes sponsa	63.4	36.6	13.2	23.5	36.0	64.0	Klekowski, *et al.* (1970)
FISH							
Phytophagous carp, *Ctenopharyngodon*	86.0	14.0	12.2	1.9	86.0	14.0	Fischer (1970)
Predatory perch, *Perca fluviatilis*	64.2	35.8	16.2	19.5	45.5	54.5	Klekowski, *et al.* (1970)

[a] Methods of analysis and experimental conditions vary greatly and are comparable only approximately.

3.10.3 Death Rate, D_z

3.10.3.1 Factors Affecting D_z

The second term in Equation (3-127) involves the zooplankton death rate, D_z. Several factors mediate D_z. These include predation by other zooplankton, predation by organisms in higher trophic levels (especially fish), endogenous respiration, mortality due to nonoptimal ambient conditions, and natural mortality. All of these are, in turn, influenced by temperature.

Predation by other zooplankton is very important in zooplankton population dynamics. Several common types are carnivorous and consume other zooplankton. The predator-prey relationships among the zooplankton are very important in determining which species predominate over time. Carnivorous zooplankton which prey on other zooplankton include species of the following genera:

- Asplanchna (rotifer)

- Polyphemus
- Leptodora

(cladocerans)

- Macrocyclops
- Acanthocyclops
- Cyclops
- Mesocyclops

(cyclopoid copepods)

The degree of predation on any zooplankton prey depends upon the degree of selectivity of the predator (willingness to take other forms) antecedent abundance of the prey species and/or other food sources, and in general, conditions affecting the growth of the predator which are exactly analogous to those affecting the prey species itself.

Predation by fish is another important sink to zooplankton biomass. Recent studies have implicated planktivorous fishes in determining, to a large extent, the dominant species of zooplankton. Often, larger zooplankton are favored by the fish, and intense grazing can lead to dominance of small zooplankton species. Studies have shown, further, that the dominance cannot be attributed to food supply (Wetzel, 1975). Wetzel also notes that the planktivorous rainbow trout (Salmo gaerdneri) and the yellow perch (Perca flavescens) cannot remove from the water zooplankton smaller than 1.3 mm. Apparently, planktivorous fishes are selective feeders, seeking out desirable food forms.

Some species of fish are obligate planktivores (e.g., the alewife, Alosa pseudoharengus) while some can prey on plankton or other types of food (trout and perch) (Wetzel, 1975).

The remaining sinks to zooplankton biomass are endogenous respiration and mortality. Endogenous respiration is the autoconsumption of zooplankton biomass in providing for organism energy needs. Mortality may be simply the result of organism aging. Nonoptimal conditions may make mortality a significant sink of zooplankton biomass. Stresses such as toxic substances, nonoptimal temperatures, and insufficient oxygen supply may cause a rapid die-off of zooplankters.

Temperature also influences rates of predation by influencing such factors as prey swimming speeds and avoidance ability, abundance of predators, physical condition of both predators and prey, and availability of alternate food supplies for predators.

3.10.3.2 Formulations for Computing D_Z

The zooplankton death rate, D_Z, is generally considered to be a function of the following processes: 1) endogenous respiration, 2) grazing by higher trophic levels, and 3) natural mortality. The mortality rate is that fraction of the biomass which is converted to detritus by death of the particular zooplankton type.

Thomann, et al. (1975) express the death rate as a function of two primary factors: 1) endogenous respiration, and 2) predation by higher trophic levels. They proposed the following general expression to describe the zooplankton death rate (D_Z, 1/day):

$$D_z = K_3(T) + K_4 \tag{3-139}$$

where $K_3(T)$ = endogenous respiration rate, a function of temperature $(\text{day-}^\circ\text{C})^{-1}$

K_4 = death rate attributed to higher trophic levels, day^{-1}

The death term due to predation by higher trophic levels, K_4, is concerned primarily with carnivorous zooplankton. The authors report that there is much uncertainty about the mechanisms involved in this process and the specific term used is empirically determined.

The death rate formulation used by Baca and Arnett (1976) is of the following form:

$$D_z = R_z + F_z \tag{3-140}$$

where R_z = endogenous respiration rate, day^{-1}

F_z = death rate due to fish predation, day^{-1}

Chen and Wells (1975) and the U.S. Army Corps of Engineers (1974) propose a zooplankton death rate expression of the following general form:

$$D_z = ZM + ZR + \frac{ZGRAZ}{PEFF \cdot ZOO} \qquad (3\text{-}141)$$

where ZM = zooplankton mortality rate, day^{-1}

ZR = zooplankton respiration rate, day^{-1}

ZGRAZ = rate of grazing on zooplankton, mg/l-day

PEFF = digestive efficiency of zooplankton grazer

ZOO = zooplankton concentration, mg/l

Canale, et al. (1976) proposed the following expression for zooplankton:

$$D_z' = \begin{bmatrix}\text{respiration} \\ \text{loss}\end{bmatrix}_z + A14_z(t)C_z \qquad (3\text{-}142)$$

where D_z' = zooplankton biomass loss due to respiration and death, mg/l-day

$A14_z(t)$ = zooplankton natural death rate, a function of temperature, day^{-1}

C_z = zooplankton concentration, mg/l

Similarly, Kelly (1975), in his model application to the Delaware Estuary, considered the zooplankton specific death rate to be a function of endogenous respiration, zooplankton death, and predation. In the Lombardo and Franz model (Lombardo, 1973), the zooplankton specific death rate is considered to be a function of respiration and natural death. Respiration is taken as a linear function of temperature, and death is considered to occur at a constant rate.

3.10.3.3 Death Rates Data

Table 3-52 provides zooplankton respiration and mortality data from a variety of studies. Tables 3-53 and 3-54 contain respiration rate data.

3.10.3.4 Measuring Zooplankton Rate Constants

Because of the tremendous diversity of ambient conditions and complexities of zooplankton population dynamics, no specific recommendations can be made here for measuring rate constants. The reader is referred to references cited in appropriate portions of the preceding text.

TABLE 3-52. VALUES FOR COEFFICIENTS IN ZOOPLANKTON SPECIFIC DEATH RATE EXPRESSIONS

Zooplankton Description	Zooplankton Respiration Rate (days^{-1})	Zooplankton Mortality Rate (days^{-1})	Location of Study	Reference
Zooplankton	0.005-0.3	-	-	Baca and Arnett (1976)
Zooplankton	0.005-0.02	0.02	North Fork Kings River, California	Tetra Tech, Inc. (1976)
Zooplankton	0.001-0.10	0.005	-	U.S. Army Corps of Engineers (1974)
Zooplankton	0.01	-	Lake Washington	Chen and Orlob (1975)
Adult Zooplankton	0.06	-	Lake Michigan	Canale, et al. (1976)
Nauplii Zooplankton	0.04	-	Lake Michigan	Canale, et al. (1976)
Copepods	-	0.003-0.005	Lake Michigan	Canale, et al. (1976)
Zooplankton	0.075	-	San Joaquin River, California	O'Connor, et al. (1975)
Zooplankton	0.10	-	San Joaquin River, Delta Estuary, California	O'Connor, et al. (1975)
Zooplankton	-	-	Potomac Estuary	O'Connor, et al. (1975)
Zooplankton	0.16	-	Lake Erie	O'Connor, et al. (1975)
Zooplankton	0.02	-	Lake Ontario	O'Connor, et al. (1975)
Zooplankton	0.36	-	-	Lombardo (1972)
Zooplankton	0.01	-	Boise River, Idaho	Chen and Wells (1975)
Zooplankton	0.01	-	San Francisco Bay Estuary	Chen (1970)

TABLE 3-53. ENDOGENOUS RESPIRATION RATES OF ZOOPLANKTON (AFTER DI TORO, *ET AL*., 1971)

Organism	Temperature °C	Respiration Rate, ml O_2/ Mg Dry Wt-Day
Cladocerans	18	14-2
	4	2.7
Copepods	18	12.2
	4	3.8
Copepods	18	8.2
	16	6.5
	12	5.2
	8	4.1
	4	3.4
Calanus finmarchicus	20	4.2
	15	2.3
	10	1.4
	4	1.3
Diaptomus leptopus	25	12.1
	20	7.4
	15	5.3
	10	2.8
	5	2.5
D. clavipes	25	12.5
	20	8.5
	15	5.1
	10	2.4
	5	1.8
D. siciloides	25	21
	20	13.5
	15	7.8
	10	5.5
	5	4.8
Diaptomus sp.	25	4.3
	20	3.0
	15	2.1
	10	1.7
	5	1.1

TABLE 3-54. VALUES FOR ENDOGENOUS RESPIRATION RATES OF ZOOPLANKTON (AFTER LOMBARDO, 1972)

Organism	Temperature, °C O_2 Consumed, μl/mg-hr Respiration rate, per hour				
Diaptomus siciloides	5° 4.42 .00563	10° 5.26 .00658	15° 9.92 .0122	20° 16.0 .0193	25° 24.4 .0288
D. oregonensis	3.88 .00495	4.71 .0059	8.65 .0106	13.8 .0167	21.0 .0248
D. leptopus	2.33 .00297	3.06 .00382	5.07 .00625	7.76 .00938	11.7 .0138
D. clavipes	2.14 .00273	2.85 .00356	4.64 .00571	7.05 .00852	10.6 .0125
D. articus	.982 .00125	1.48 .00185	2.06 .00254	2.93 .00354	4.38 .00577
Acartia clausi[1]		10° 13.0 .0162	13° 12.4 .0154	17° 15.8 .0193	20° 18.9 .0229
Centropages hamatus[2]	2.27 .00288	4.54 .00568	6.34 .00786	7.56 .00922	
Temora longicornis[3]		10° 5.4 .00675	13° 5.4 .0067	17° 7.2 .00878	20° 10.3 .0125
Daphnia magna		3.4 .00425			5.4 .00654
Copepods (*Diaptomus* and *Cyclops*)	4° 3.3 .00422	8° 4.3 .00541	12° 5.7 .00707	16° 6.6 .00811	19° 8.07 .00977
Copepods (*Diaptomus* and *Cyclops*)	3.8 .00487				12.2 .0148
Cladocerans (*Ceriodaphnia* and *Daphnia*)	2.7 .00346				14.2 .0172

[1] Mean length 0.85 mm; assumed weight 0.005 mg/animal

[2] Mean length 0.89 mm; assumed weight 0.015 mg/animal

[3] Mean length 0.787 mm; assumed weight 0.015 mg/animal

3.10.4 Summary

Zooplankton populations in surface water bodies tend to be ephemeral over time, with population dynamics being dependent upon food availability, temperature, and abundance of predators. Because of the importance of zooplankton in phytoplankton population dynamics, zooplankton are normally simulated in surface water ecomodels. Modeling is usually of a form similar to that for phytoplankton - that is, zooplankters grow, respire, and die. Michaelis-Menton formulations are commonly used in computing growth rates with primary application in terms of phytoplankton availability. Despite the complex population dynamics in the plankton communities, a simple representation of fish grazing on zooplankton and zooplankton grazing on phytoplankton is commonly used.

3.10.5 References

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